Cohesive properties of iron obtained by use of the generalized gradient approximation

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Cohesive and magnetic properties of bcc, fcc, and hcp Fe are calculated by use of the generalized gradient approximation proposed by Perdew and Wang [Phys. Rev. B **33**, 8800 (1986)] and Perdew [Phys. Rev. B **33**, 8822 (1986)]. Calculated results reproduce most of the fundamental cohesive properties found experimentally. For example, the pressure-induced phase transition between bcc ferromagnetic and hcp nonmagnetic phases can be successfully described.

The local-density approximation (LDA) in the density-functional theory[1] has enjoyed considerable success during the last few decades.[2] From its high feasibility and overall reliability, the importance of its role in the calculation of ground-state properties seems to remain almost unchanged. It is, however, well known that the LDA sometimes gives unsatisfactory results compared with experimental ones. For example, it predicts overbound cohesive quantities for $3d$ metals with cohesive energies that are larger by about 10% and interatomic distances that are smaller by a few percent. More seriously, it cannot give the correct ground state of the bcc-ferromagnetic (FM) phase for Fe.[3]

Improvement of the LDA has been undertaken from several standpoints. Among them, the gradient correction method introduces corrections by adding effects from the electron-density gradient (hopefully from higher derivative terms also). Belonging to a family of the generalized local approximation,[4] this method has great advantages in scarcely destroying the virtue of feasibility of the LDA. Following this line, Perdew and Wang[5] and Perdew[6] proposed a formalism named the generalized gradient approximation (GGA). They showed that for atoms the new functional could correct most of the errors in the exchange and correlation energies by LDA. The first application of the GGA to solids was done by Bagno, Jepsen, and Gunnarsson.[7] Strikingly, they showed that the new functional could reproduce correctly the bcc-FM phase for the ground state of Fe. Kong *et al.*[8] calculated cohesive properties of Al, C, and Si with sizable improvements especially in cohesive energy. Later Barbiellini, Moroni, and Jarlborg[9] carried out an extensive test of the functional to find out its consequences on cohesive, magnetic, and Fermi surface properties on a wider variety of metals. Contrary to the favorable findings of the former two, they found that the GGA results were sometimes inferior to those of the LDA, especially for $4d$ and $5d$ metals. The effects of the new functional, a distinguished one of which is its inclination for expanding lattice spacing, worked too much for $4d$ and $5d$ metals, whose lattice constants had already been given more or less satisfactorily well by the LDA.

In spite of the negative features found by Barbiellini, Moroni, and Jarlborg,[9] the improvements achieved for cohesive properties of $3d$ metals[10] or lighter elements should be properly appreciated. The purpose of the present paper is to clarify the extent to which the GGA can claim its success for Fe by a thorough search on its fundamental structures of lattices and magnetic phases and thus to contribute to a refinement of GGA. We limited lattices to bcc, fcc, and ideal hcp and magnetic phases to nonmagnetic (NM), FM, and antiferromagnetic (AF).[11] The results presented here were calculated by the linear muffin-tin orbital (LMTO) method[12] in the atomic sphere approximation (ASA) with the so-called combined correction. Relativistic effects were taken into account by the scalar form[13] for both core and valence states. The basis consisted of *spdf*-LMTO's. We employed the linear tetrahedron method[14] for sampling k points and each eigenstate was weighted by the Fermi distribution function with a broadening factor of 1 mRy. For the NM or FM phase of bcc (fcc) lattice, we employed a unit cell which contained two atoms, i.e., simple cubic (sc) [body-centered tetragonal (bct)] unit cell, the one for the AF phase, in order to avoid possible errors of ~ 1 mRy introduced in handling different unit cells for different magnetic phases. The numbers of irreducible k points were 220 for sc and 216 for bct, and 180 for the hcp lattice. Common lower-cutoff radii for the radial integrations were chosen for all calculations since the total energy by the GGA does not converge with respect to the cutoff radius. The c/a was chosen to be ideal ($=1.633$) for the hcp lattice. The Ceperley-Alder exchange-correlation functional[15] was employed for LDA. The effect of the zero-point motion is not taken into account for simplicity. Quantities such as the equilibrium Wigner-Seitz radius R_{WS}, cohesive energy E_{coh}, and bulk modulus B, were obtained by the least-mean-squares fitting of the calculated total energies to the Murnaghan equation of state.[16] Since the value of the magnetic moment was not fixed in the self-consistent field iterations, the iterations, sometimes for the case of possible appearance of two spin states, became very intractable for either one or both of two spin states. Branches shown in this paper are those

whose convergences were strictly achieved. The small spin states were identified as NM if values of the magnetic moment μ were effectively zero (less than $\sim 0.05\mu_B$) throughout a certain R_{WS} range. In this paper we call a small spin branch the low-spin (LS) branch only when it is judged to be discontinuously connected to the high-spin (HS) branch in the $R_{WS}-\mu$ diagram.

Relevant experimental facts to be compared with the present calculation are summarized as follows.

(1) Under zero pressure, the ground state of Fe is bcc-FM, with $R_{WS}=2.66$ a.u., $B=1.68$ kbar, $E_{coh}=0.317$ Ry, and $\mu=2.12\mu_B$.[17] Next follows the hcp phase. The fcc (NM or AF) phase seems to exist above the hcp phase.[18]

(2) Under an increasing pressure , bcc-FM to hcp-NM phase transition occurs at a pressure of ~ 150 kbar (Ref. 19) at low temperature. At the transition point R_{WS} is ~ 2.61 a.u. on the bcc-FM phase and ~ 2.56 a.u. at the hcp-NM (Ref. 20) phase with $c/a \sim 1.60$.

(3) For the fcc phase, two experimental observations under bulk environments have been made on precipitates, i.e., one[21] in Cu is AF with $R_{WS}=2.65$ a.u. and $\mu \sim 0.7\mu_B$, and the other[22] in CuAu alloys is FM with $R_{WS} \sim 2.78$ a.u.

First we show in Fig. 1 the total energy E_{tot} and μ as a function of R_{WS}, calculated by the LDA. The overall features are essentially the same as those by earlier calculations.[3,7,23] The HS branch for the fcc-FM phase was not obtained in the region searched. Except for bcc-FM, the stable HS branches obtained collapse at a certain critical R_{WS}. The small-spin solutions often went finally to NM states after careful and sufficient iterations. Only one LS solution for fcc-FM was obtained. The difficulties in obtaining both HS and LS solutions in the fcc-FM phase, the absence of the LS branch in the hcp-FM phase, and the behavior of the μ change in the fcc-AF phase can be understood by the help of earlier fixed-spin-moment method calculations.[24] Though the LDA gives rather correctly mutual locations of the NM phase of three lattice structures in the $R_{WS}-E_{tot}$ diagram, it is difficult to seek agreement with the experimental facts stated above, because the LDA, along with its inclination for giving smaller lattice constants, produces magnetic energy gains that are insufficient or too small. From Fig. 1 we observe that the LDA predicts a false ground state of the hcp-NM with no possibility of the pressure-induced bcc-hcp transition nor of the existence of any stable (or metastable) AF or FM phases in the required R_{WS} range of the fcc lattice.

Figure 2 shows the GGA results of E_{tot} and μ as a function of R_{WS}. The HS branches were stably obtained for FM and AF phases of all three structures. The LS branch was obtained only for the hcp-AF phase. Compared with Fig. 1, we can list characteristic features of GGA as follows: (1) it has an inclination to produce larger interatomic distances, and (2) its magnetic energy gain is significantly larger than the one by LDA. These two features come mostly from the functional form of the GGA used to evaluate the exchange-correlation energy.[25] Owing to these features, the total energy diagram shifts toward larger R_{WS} and total energies of magnetic phases lower a great deal by formation of magnetic moment. As seen in Fig. 2, the ground state of the GGA is correctly bcc-FM and corresponding equilibrium values are $R_{WS}=2.683$ a.u., $B=1.58$ kbar, and $\mu=2.32\mu_B$ and E_{coh} is 0.359 Ry. These values are essentially the same as those by Bagno, Jepsen, and Gunnarsson.[7] Compared with the experimental values listed above, R_{WS} is larger by 0.8%, E_{coh} is larger by 13%, and μ is larger by 9%. The discrepancy in the magnetic moment seems to come from the present treatment by ASA and the inclusion of the nonspherical potential will amend most of the errors.[10] We next discuss the relation between the total energy curves of bcc-FM and hcp-NM phases, which concerns the pressure-induced bcc-hcp transition at low temperature. From Fig. 2 we can expect the transition in the direction observed experimentally. The transition pressure is estimated to be 149 kbar and the critical R_{WS} at the bcc-FM side is 2.62 and 2.54 a.u. at the hcp side. The agreements of the pressure and the R_{WS}'s with the corresponding experimental values of ~ 150 kbar, 2.61 a.u., and 2.56 a.u.,[20] respectively, seem quite satisfactory. As for the fcc lattice, Fig. 2 predicts one stable AF phase

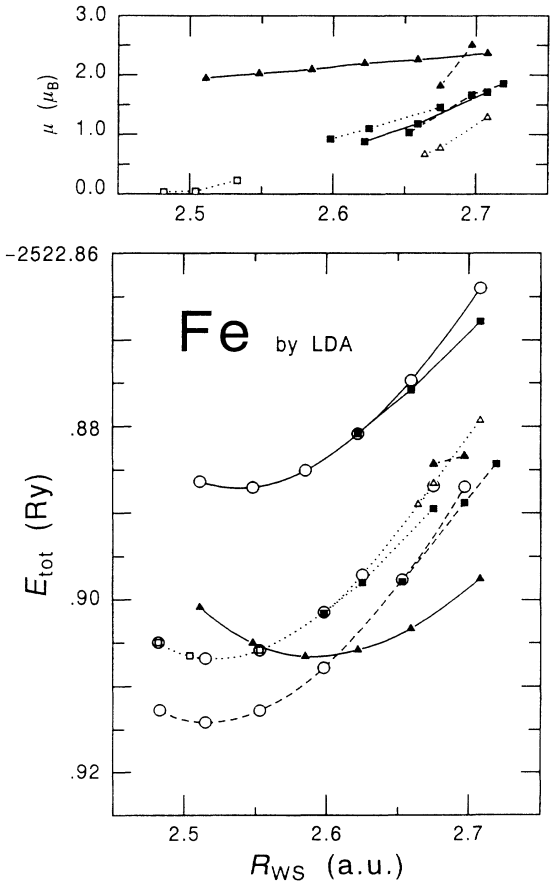

FIG. 1. Total energy E_{tot} and magnetic moment μ of Fe as a function of the Wigner-Seitz radius R_{WS}, calculated by the LDA of Ceperley and Alder. The solid curve corresponds to the bcc, the dotted to the fcc, and the dashed to the hcp. The circles indicate NM, the triangles FM, and the squares AF, and the filled (open) symbols are for the high-spin (low-spin) state solutions of the corresponding magnetic phase.

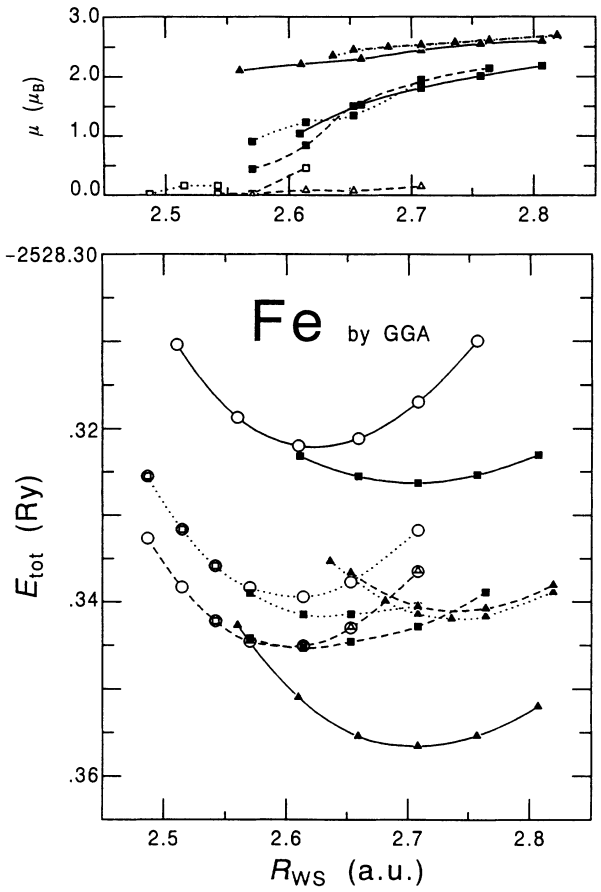

FIG. 2. Total energy E_{tot} and magnetic moment μ of Fe as a function of the Wigner-Seitz radius R_{WS}, calculated by the GGA of Perdew and Wang, and Perdew. The solid curve corresponds to the bcc, the dotted to the fcc, and the dashed to the hcp. The circles indicate NM, the triangles FM, and the squares AF, and the filled (open) symbols are for the high-spin (low-spin) state solutions of the corresponding magnetic phase.

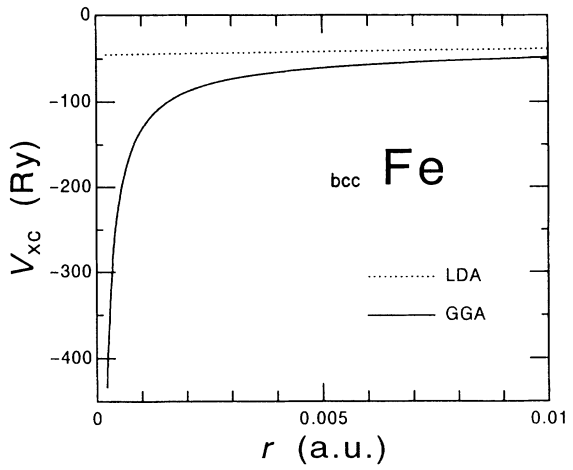

FIG. 3. Comparison of the exchange-correlation potential V_{xc} by the GGA with that by the LDA for the majority spin of the bcc Fe. The $-1/r$ divergence of the GGA exchange-correlation potential is clearly observed and makes a striking contrast to the rather flat behavior of the LDA potential.

with $\mu=1.21\mu_B$ at $R_{WS}=2.62$ a.u. and one FM with $\mu=2.56\mu_B$ at $R_{WS}=2.72$ a.u. The values of the R_{WS}'s, 2.65 and 2.78 a.u., observed on microprecipitates in Cu (Ref. 21) and CuAu alloys[22] seem to correspond to these equilibrium values. Their agreements seem to be rather good, though the theoretical magnetic moment $1.21\mu_B$ is too large compared with the experimental value of $\sim 0.7\mu_B$.[21] Finally, we mention some possibility that the electronic structure by GGA might be favorable for a description of finite-temperature behaviors of Fe. The total energy difference between the equilibrium values of fcc-AF and hcp-AF phases is 4.6 mRy, and the one between those of hcp-AF and bcc-FM phases is 7.6 mRy by the present calculation. These values correspond to 1.0 and 7.3 mRy, respectively, which were used by Hasegawa and Pettifor[26] as energy separations at absolute zero temperature in their semiquantitative treatment of the phase transition of Fe at finite temperature based on the spin-fluctuation mechanism. Taking their success into account, the quantitative agreement in these values convinces us that the GGA might provide a sound starting point for treating the finite-temperature behaviors of Fe.

So far we have shown that the GGA can reproduce satisfactorily most of the fundamental facts related to the cohesive property of Fe, i.e., quantities related to (1) the ground-state properties, (2) the pressure-induced bcc-hcp phase transition, and (3) the two equilibrium fcc phases. Therefore we believe the present calculation firmly substantiates the success of GGA shown so far by earlier workers.[7-10] It should be mentioned, however, that the Kohn-Sham exchange-correlation potential of the GGA, or generally of the gradient correction method, has $-1/r$ divergence with $r\rightarrow 0$ as illustrated in Fig. 3. It comes from terms containing $\nabla^2\rho$ with ρ the electron density, which is generated by taking the functional derivative of the gradient terms in the exchange-correlation energy density. Though this divergence little affects integrated values such as the total energy, it seems to be fatal for treating the hyperfine field: By the divergence, the wave function near the nucleus is severely affected and the hyperfine field is disturbed very much from the value by LDA with, e.g., an unphysical positive contribution from the $1s$ orbital for Fe. Removal of this divergence, together with the undesirable aspect of overestimating lattice spacings noticed particularly in $4d$ and $5d$ metals, is strongly required.

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[1]P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[2]R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).

[3]C. S. Wang, B. M. Klein, and H. Krakauer, Phys. Rev. Lett. **54**, 1852 (1985).

[4]W. Kohn, in *Density Functional Method in Physics,* Vol. 123 of *NATO Advanced Study Institute Series B: Physics,* edited by R. M. Dreizler and J. da Providencia (Plenum, New York, 1985).

[5]J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).

[6]J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).

[7]P. Bagno, O. Jepsen, and O. Gunnarsson, Phys. Rev. B **40**, 1997 (1989).

[8]X. J. Kong, C. T. Chan, K. M. Ho, and Y. Y. Ye, Phys. Rev. B **42**, 9357 (1990).

[9]B. Barbiellini, E. G. Moroni, and T. Jarlborg, J. Phys. Condens. Matter **2**, 7597 (1990).

[10]Very recent papers also confirmed the success of GGA on 3*d* metals. See, D. J. Singh, W. E. Pickett, and H. Krakauer, Phys. Rev. B **43**, 11 628 (1991); T. C. Leung, C. T. Chan, and B. N. Harmon, *ibid.* **44**, 2923 (1991).

[11]No magnetically included distortions were taken into account. Since the associated energy is small, conclusions of the present paper will not be altered by the inclusion of the lattice distortion. See, for example, T. Oguchi and A. J. Freeman, J. Magn. Magn. Mater. **46**, L1 (1984).

[12]O. K. Andersen, Phys. Rev. B **12**, 3060 (1975); H. L. Skriver, *The LMTO Method* (Springer, Berlin, 1984).

[13]D. D. Koelling and B. N. Harmon, J. Phys. C **10**, 3107 (1977).

[14]J. Rath and A. J. Freeman, Phys. Rev. B **11**, 2109 (1975).

[15]D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[16]F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **3**, 244 (1944).

[17]H. Danan, A. Harr, and A. J. P. Meyer, J. Appl. Phys. **39**, 669 (1968); W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon, Oxford, 1964).

[18]The sequence may be concluded from the pressure-volume phase diagram of Fe by recognizing that the appearance of the bcc-FM phase is due to its large magnetic energy gain. See Ref. 26.

[19]L. Kaufman, E. V. Clougherty, and R. J. Weiss, Acta Metall. **11**, 323 (1961).

[20]D. L. Williamson, S. Bukshpan, and R. Ingalls, Phys. Rev. B **6**, 4194 (1972).

[21]C. Abrahams, L. Guttman, and J. S. Kasper, Phys. Rev. **127**, 2052 (1962); G. Johanson, M. B. McGirr, and D. A. Wheeler, Phys. Rev. B **1**, 3208 (1970).

[22]U. Gonser, K. Krishel, and S. Nasu, J. Magn. Magn. Mater. **15-18**, 1145 (1980).

[23]J. Kübler, Phys. Lett. **81A**, 81 (1981); H. J. F. Jansen, K. B. Hathaway, and A. J. Freeman, Phys. Rev. B **30**, 6177 (1984).

[24]V. L. Moruzzi, P. M. Marcus, K. Schwarz, and P. Mohn, Phys. Rev. B **34**, 1784 (1986); V. L. Moruzzi, P. M. Marcus, and J. Kübler, *ibid.* **39**, 6957 (1989); M. Podgórny and J. Goniakowski, *ibid.* B **42**, 6683 (1990).

[25]Pertubative evaluations of the exchange-correlation energy of Fe by use of a converged LDA electron density recovers most of the total energy difference of ~ 6 Ry between those of LDA and GGA. A remaining small difference (~ 7 mRy) is amended by redistribution of electron density. The first feature in the text is easily perceived from the functional form of the GGA exchange-correlation energy density, Ref. 5: The GGA correction to the exchange (correlation) energy density is a negative (positive) and ever decreasing (increasing) function of the quantity s with $s \propto |\nabla\rho|/\rho^{4/3}$, where ρ is the electron density. Since the magnitude of the correction to the exchange part is several times larger than that to the correlation part, the total correction to the exchange-correlation energy density is a negative ever decreasing function of s. Since ρ decreases and $|\nabla\rho|$ increases for lattice expansion in general, the quantity s increases with the expansion, which leads to the first feature. For the second feature in the text, it is not straightforward to explain it simply from the functional form. We hope its generality will be confirmed numerically by further examples. It might be conceived that the feature might come from the enhancement of the magnetic moment. But it should be generally denied since the feature stands also for the GGA full-potential calculation where the magnetic moment is reduced from the one by LDA (see Singh, Pickett, and Krakauer of Ref. 10).

[26]H. Hasegawa and D. G. Pettifor, Phys. Rev. Lett. **50**, 130 (1983).