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Generalized-gradient-approximation study of the magnetic and cohesive properties of bcc, fcc, and hcp Mn

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Magnetic and cohesive properties of bcc, fcc, and ideal hcp Mn 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 predict correctly an antiferromagnetic ground state for the fcc structure with lattice constant and magnetic moment in good agreement with experimental values. An investigation of the contribution to the free energy from lattice vibration by use of the quasiharmonic approximation removes apparent difficulties involving an hcp ground state in the calculated total energies of three structures.

The generalized gradient approximation (GGA) proposed by Perdew and Wang[1] for the exchange energy and by Perdew[2] for the correlation energy has been tested by an increasing number of workers. It was shown that the new functional improved considerably the total energies of atoms[1-3] and molecules[4,5] and the cohesive properties of solids formed by $3d$ and lighter elements.[3,6,7,10] It is now well accepted that this functional correctly predicts the bcc ferromagnetic (FM) phase for the ground state of Fe.[6,7] In our recent paper,[8] cited as I hereafter, we have substantiated the success with Fe by demonstrating that most of the fundamental cohesive properties of Fe could be reproduced satisfactorily by use of the GGA. However it is also well known that for $4d$ and $5d$ metals[7,10] the results obtained by use of GGA are worse than those of the local-density approximation (LDA) in density-functional theory.[9] It was recently reported[11] that the GGA pseudopotential calculation of Al, Si, Ge, and other atoms gave no consistent improvement over results by LDA especially for lattice constants and bulk moduli. Therefore, the reputation of GGA seems somehow controversial at the present stage. In this work we extend the investigation carried out in I to Mn and give a further assessment of GGA. We calculate the total energy and magnetic moment for simple fundamental lattice structures and give comparisons with experimental results by taking the finite-temperature effects of the lattice vibration into account. Preliminary reports of the present work have been submitted elsewhere.[12,13]

As in I, we limited lattices to bcc, fcc, and ideal hcp and magnetic phases to nonmagnetic (NM), ferromagnetic (FM), and antiferromagnetic (AF) phases. For the AF phase we assumed a spin ordering reported for fcc AF Mn,[14] where the magnetic moments in a (001) plane are parallel to each other but antiparallel to those in alternate sheets. No modulations in the lattice structure cauesd by magnetic ordering were taken into account. We employed the linear muffin-tin orbital (LMTO) method[15] in the atomic-sphere approximation (ASA) with the so-called combined correction. Relativistic effects were taken into account by the scalar form[16] for both core and valence states. The basis consisted of *spdf* LMTO's. We used the linear tetrahedron method[17] 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) structure, 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 some mRy introduced in handling different unit cells for different magnetic phases. The numbers of irreducible k points were 165 for sc and 140 for bct and hcp structures. The Ceperley-Alder exchange-correlation functional[18] was employed for LDA.

Mn occurs in four allotropic forms, i.e., α, β, γ, and δ phases, with increasing temperature and at atmospheric pressure.[19] The first two phases, α and β, have complex structures with 29 and 20 atoms per unit cell, respectively. The α phase exists up to $\sim$1073 K. The γ (δ) phase is simple fcc (bcc) and occurs between $\sim$1373 (1407) and 1407 ($\sim$1518) K. The γ phase can be quenched to room temperature and it is known that the magnetic structure is AF with magnetic moment μ equal to $2.30\mu_B$, the Wigner-Seitz radius $r_{\rm WS}$ equal to 2.752 a.u. (at room temperature), and that the Néel temperature $T_N=540$ K (Ref. 20) and $r_{\rm WS}=2.853$ a.u. at 1373 K.[19] For the bcc structure $r_{\rm WS}$ is 2.867 a.u. at 1413 K (Ref. 19) and its magnetic structure has not been manifested yet.

Figure 1 shows the LDA results of total energy $E_{\rm tot}$ and μ as functions of $r_{\rm WS}$. The result for each of the bcc and fcc structures is essentially the same as the corresponding one reported earlier.[21] At $r_{\rm WS}\sim 2.59$ a.u. around which all phases have their minimum energies, we obtained only one magnetic branch of bcc FM which is almost degenerate to the NM one. The lowest-energy phase among these three structures is hcp NM with 6.5-mRy difference to the next lowest bcc. The difference between the bcc and fcc minima is 0.5 mRy. Compared with experimental results, LDA gives too small lattice constants and cannot predict an AF phase for the ground state of the fcc structure. LDA would predict the hcp NM phase, rather than that of fcc or bcc, for the high-

temperature phase if we estimated the most stable state by taking the effect of lattice vibration into account by the way we will show later.

In Fig. 2 we show a GGA counterpart of Fig. 1. Compared with Fig. 1, we perceive that the magnetic energy gain brings about sizable effects on the total energies of the magnetic branches. Findings on the results of Fig. 2 are as follows.

(1) For the hcp structure, the ground state is AF with $r_{WS}=2.654$ a.u. and $\mu=0.20\mu_B$, whose total energy is marginally lower than that of the NM phase. FM solutions are found for r_{WS}'s greater than ~ 2.85 a.u.

(2) For the fcc structure, the ground state is AF with $r_{WS}=2.718$ a.u. and $\mu=2.13\mu_B$. We will show that their theoretical values at room temperature given later agree well with corresponding experimental values. The total-energy difference with that of the next-lowest NM is 3.4 mRy, which definitely supports the experimental finding of AF for the ground state of this structure.

(3) For the bcc structure, the ground state is FM with $r_{WS}=2.669$ a.u. and $\mu=0.99\mu_B$. The NM minimum with $r_{WS}=2.658$ a.u. is located 1.4 mRy above the FM minimum and the AF minimum lies 3.5 mRy further above the NM one with $r_{WS}=2.797$ a.u. and $\mu=2.73\mu_B$.

(4) The most stable phase among those investigated is hcp AF. The total-energy difference between hcp AF and the next-lowest fcc AF is 3.0 mRy. Our concerns here are whether the crystal structure and magnetic phase predicted to appear at high temperature agree with the experimental fact, since the hcp structure is not observed in any temperature region for pure Mn, and the prediction of r_{WS}'s of fcc and bcc AF phases for which we have experimental results.

To explore how the branches of Fig. 2 evolve with temperature, we investigate the effect of the lattice vibration by using the quasiharmonic approximation.[22] We limit the investigation within a certain low-temperature range sufficiently below the magnetic transition temperature, since the electronic structures we are based on for magnetic branches are those for completely ordered states. Leaving a study of the contribution by the spin fluctuation to the free energy as a future task, here we point out specifically a possibility that the lattice vibration plays an important role in the phase stability at finite temperatures. By the quasiharmonic approximation, the free en-

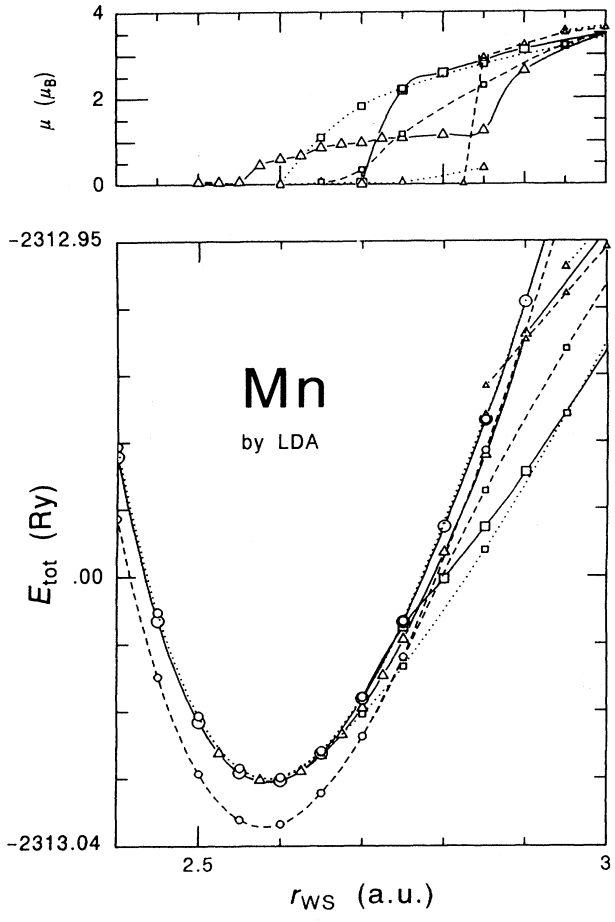

FIG. 1. Total energy E_{tot} and magnetic moment μ of Mn as functions of r_{WS}, calculated with Ceperley-Alder LDA functional. The zero-point energy is not included. The solid curve corresponds to the bcc structure, the dotted to the fcc, and the dashed to the hcp. The circles indicate NM, the triangles FM, and the squares AF.

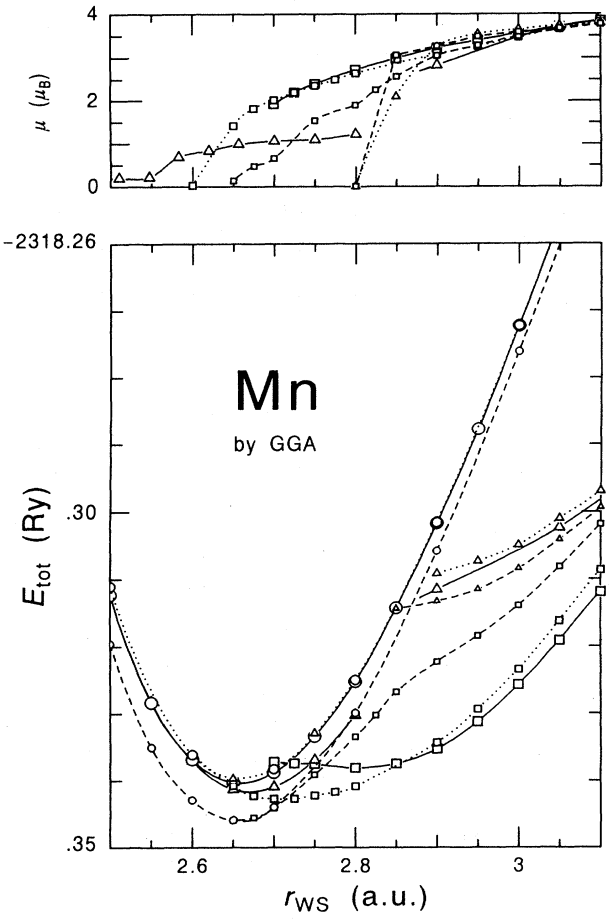

FIG. 2. Total energy E_{tot} and magnetic moment μ of Mn as functions of r_{WS}, calculated by GGA. For explanations, see Fig. 1.

ergy F as a function of r_{WS} and temperature T can be expressed as follows:

$$F(r_{WS},T)=E_{tot}(r_{WS}) -k_BT\{D(\Theta_D/T)-3\ln(1-e^{-\Theta_D/T})\} +\tfrac{9}{8}k_B\Theta_D\ , \quad (1)$$

where Θ_D is the Debye temperature and $D(x)$ is the Debye function. In Eq. (1) an electronic contribution in entropy and internal energy change at finite temperature is neglected since it would be much smaller compared with the one from the phonon part except at very low temperature. The last term of Eq. (1) represents the zero-point energy. $(\Theta_D)_0$, the Debye temperature for an equilibrium Wigner-Seitz sphere radius $(r_{WS})_0$, is expressed by $c[(r_{WS})_0B_0/M]^{1/2}$ where B_0 is the bulk modulus B for $(r_{WS})_0$ and M is the atomic mass. For the coefficient c, Morruzi, Janak, and Schwarz[22] used 41.63 by specifying r_{WS} in a.u., B in kbar, and M in proton mass. Since there exist no experimental values available for judging the adequacy of the value for the structures investigated here, we employ their value in this paper.[23] In Eq. (1), the r_{WS} dependence of the phonon part enters by way of Θ_D assuming that it varies with $(r_{WS})^{-3\gamma}$, where γ, the Grüneisen constant, is given by use of the pressure derivative of B at an equilibrium r_{WS}, B_0', as $B_0'/2-d$. The constant d is chosen to be $\frac{1}{2}$ at low temperature and $\frac{1}{6}$ at sufficiently high temperature where all vibrational modes are excited. We give the value of d for a specified temperature by linearly interpolating d between $\frac{1}{2}$ (0 K) and $\frac{1}{6}$ (1518 K). The quantities B_0, B_0', and $(r_{WS})_0$, for T, are obtained by least-mean-squares fitting $F(r_{WS},T)$ to the Murnaghan equation of states,[24] which means that these quantities are to be self-consistently determined since $F(r_{WS},T)$ itself is expressed by use of these quantities.[25]

The free energy (lattice constant) lowers (increases) more rapidly with increasing temperature for the phase which has a smaller bulk modulus (positive larger Grüneisen constant) in Fig. 2. Quantities at $T=0$ K such as the minimum value of total energy, $(E_{tot})_{min}$, B_0, γ, $(r_{WS})_0$, and μ, obtained for relevant branches of Fig. 2 are listed in Table I. We notice that phases which become important at high temperature are those of bcc AF and fcc AF. For the bcc AF phase the Grüneisen constant is negative, which inevitably predicts a singular negative thermal expansion coefficient. This negative value of the Grüneisen constant comes from the abnormally flat total-energy curve in the smaller r_{WS} (higher pressure) region.[26] In Fig. 3 we show the change of the free energy F for the four branches listed in Table I. We limit the temperature range below 500 K by the reason stated above. In the figure we observe first that the hcp AF phase is replaced by the fcc AF phase as the lowest free-energy phase at rather low temperature ~300 K. Since there must surely exist the more stable α phase at low temperature, the hcp structure will never be realized, if not stabilized by, e.g., alloying or with some structure-forcing technique like molecular-beam epitaxy. This situation

TABLE I. Quantities derived from total-energy curves of Fig. 2. The total-energy minimum $(E_{tot})_{min}$ is in Ry, measured from −2318 Ry, bulk modulus B_0 in Mbar, Wigner-Seitz radius $(r_{WS})_0$ in a.u., and magnetic moment μ in μ_B. γ means the Grüneisen constant. The subscript 0 stresses that these quantities are of equilibrium in accordance with the definition in the text.

		$(E_{tot})_{min}$	B_0	γ	$(r_{WS})_0$	μ
bcc	AF	−0.3381	0.77	−0.72	2.799	2.73
	FM	−0.3416	2.48	2.73	2.669	0.99
fcc	AF	−0.3429	1.07	3.32	2.716	2.13
hcp	AF	−0.3459	2.64	2.79	2.654	0.02

meets the experimental facts. Next we observe that the AF phase is the most stable one for the bcc structure for temperatures higher than ~300 K. The calculated values of r_{WS} and μ at 300 K for the fcc AF phase are 2.775 a.u. and $2.37\mu_B$, respectively, and they agree well with the corresponding experimental one of 2.752 a.u. and $2.30\mu_B$. For the bcc structure no such comparisons are possible since the bcc phase exists only near the melting point. A straightforward evaluation of the free energy by the present scheme at temperatures high up to the melting point suggests that the lattice vibration might play an important role for the experimental occurrence of the fcc-bcc conversion. We await the investigation of the high-temperature behaviors of these magnetic phases which takes the effects of both lattice vibration and spin fluctuation into account.

Here we briefly mention the consequence of magnetically induced distortion which has been discarded in the present work. Experimentally it was observed for the fcc AF phase[20] that below T_N, the fcc lattice showed a tetragonal distortion of about a 6% contraction along the [001] axis, which was considerably larger than the case of fcc Fe.[27] The energy lowering by this distortion was calculated to be ~1 mRy by the LMTO-ASA method,[28]

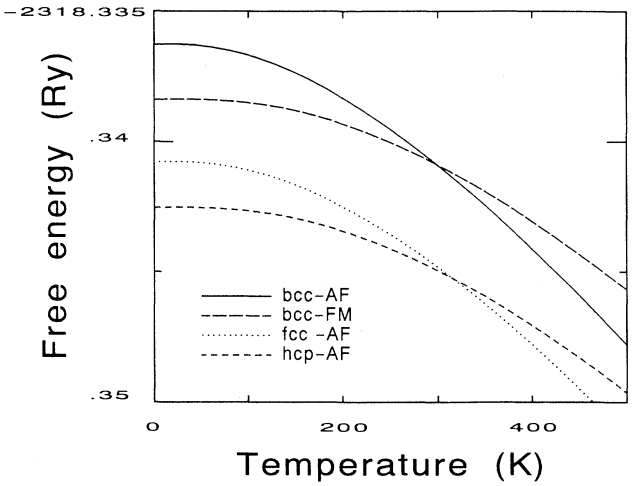

FIG. 3. Free energy of bcc AF, bcc FM, fcc, and hcp AF phases as a function of temperature calculated by quasiharmonic approximation.

which may give a rough estimation of its consequence. A similar but probably smaller energy gain may also be associated with the hcp AF and bcc AF phases. Since these energy gains are of the same order as the total-energy difference between four participating phases in Fig. 2, the inclusion of the distortion might affect to some extent the relative location of these ground-state energies and thus the predicted temperatures of hcp-fcc and fcc-bcc crossovers. However, we will be safe in the present conclusion on the replacement of the hcp phase by the fcc AF at rather low temperature, since the difference in the values of B_0 for two phases determined the occurrence almost decisively.

We have performed the total-energy calculation as a function of lattice spacing for Mn by use of both LDA and GGA for the fundamental crystal and magnetic structures. The AF phase has been found to be the ground state of the fcc structure with the lattice spacing and magnetic moment in good agreement with the experiment. The investigation of finite temperature behaviors by the quasiharmonic approximation has found that an apparent difficulty which involves the hcp ground state would cause no trouble at high temperature in comparison with the experimental fact. We believe that the present results confirm the success of GGA on Fe shown by I.

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[1]J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).
[2]J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).
[3]X. J. Kong, C. T. Chan, K. M. Ho, and Y. Y. Ye, Phys. Rev. B **44**, 2923 (1991).
[4]F. W. Kutzler and G. S. Painter, Phys. Rev. Lett. **59**, 1285 (1987); Phys. Rev. B **37**, 2850 (1988).
[5]K. Kobayashi, N. Kurita, H. Kumahora, and K. Tago, Phys. Rev. A **43**, 5810 (1991).
[6]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); T. C. Leung, C. T. Chan, and B. N. Harmon, *ibid.* **44**, 2923 (1991); J. Häglund, *ibid.* **47**, 566 (1993).
[7]B. Barbiellini, E. G. Moroni, and T. Jarlborg, J. Phys. Condens. Matter **2**, 7597 (1990).
[8]T. Asada and K. Terakura, Phys. Rev. B **46**, 13 599 (1992).
[9]P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).
[10]M. Körling and J. Häglund, Phys. Rev. B **45**, 13 293 (1992).
[11]A. García, C. Elsässer, J. Zhu, S. G. Louie, and M. L. Cohen, Phys. Rev. B **46**, 9829 (1992).
[12]T. Asada and K. Terakura, in *Computer Aided Innovation of New Materials II,* edited by M. Doyama, J. Kihara, M. Tanaka, and R. Yamamoto (Elsevier, Amsterdam, 1993), p. 169.
[13]T. Asada, in *Interatomic Potential and Structural Stability,* edited by K. Terakura and H. Akai (Springer-Verlag, New York, in press).
[14]D. Meneghetti and S. S. Sidhu, Phys. Rev. **105**, 130 (1957).
[15]O. K. Andersen, Phys. Rev. B **12**, 3060 (1975); H. L. Skriver, *The LMTO Method* (Springer, Berlin, 1984).
[16]D. D. Koelling and B. N. Harmon, J. Phys. C **10**, 3107 (1977).
[17]O. Jepsen and O. K. Andersen, Solid State Commun. **9**, 1763 (1971); J. Rath and A. J. Freeman, Phys. Rev. B **11**, 2109 (1975).
[18]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).
[19]R. W. G. Wyckoff, *Crystal Structure* (Wiley, New York, 1963), Vol. 1, p. 50.
[20]Y. Endoh and Y. Ishikawa, J. Phys. Soc. Jpn. **30**, 1614 (1971).
[21]J. L. Fry, Y. Z. Zhao, N. E. Brener, G. Fuster, and J. Callaway, Phys. Rev. B **36**, 868 (1987); V. L. Moruzzi, P. M. Marcus, and P. C. Pattnaik, *ibid.* **37**, 8003 (1988); S. Fujii, S. Ishida, and S. Asano, J. Phys. Soc. Jpn. **60**, 1193 (1991); G. Fuster, N. E. Brener, J. Callaway, J. L. Fry, Y. Z. Zhao, and D. A. Papaconstantopoulos, Phys. Rev. B **38**, 423 (1988); V. L. Moruzzi, P. M. Marcus, and J. Kübler, *ibid.* **39**, 6957 (1989); M. Podgórny and J. Goniakowski, *ibid.* **42**, 6683 (1990).
[22]V. L. Moruzzi, J. F. Janak, and K. Schwarz, Phys. Rev. B **37**, 790 (1988).
[23]In Ref. 22 Morruzi, Janak, and Schwarz obtained the value of 41.63 on the basis of linearities between B and longitudinal and shear moduli found experimentally on some selected materials. For $3d$ metals, the values of Θ_D estimated by use of the value and experimental r_{WS} and B differ considerably from those derived experimentally. For example, the ratios of theoretical to experimental are 0.65 (Cr), 0.79 (bcc Fe), 0.84 (Ni), and 0.93 (Cu). Therefore, we checked the calculations of temperature dependence as shown in the text with three different values, 0.8×41.63, 41.63, and 1.2×41.63. We found no significant differences in these three calculations as to require essential changes in the conclusions stated in the text.
[24]F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **3**, 244 (1944).
[25]The consequence of self-consistency was found to be small for the present cases.
[26]We have carried out far more than enough iterations especially for this branch.
[27]Y. Tsunoda and N. Kunitomi, J. Phys. F **18**, 1405 (1988).
[28]T. Oguchi and A. J. Freeman, J. Magn. Magn. Mater. **46**, L1 (1984).