Ground-state properties of Fe, Co, Ni, and their monoxides: Results of the generalized gradient approximation

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The lattice parameter, bulk modulus, cohesive energy, and magnetization of Fe, Co, and Ni are calculated using the generalized gradient approximation (GGA) of Perdew and co-workers. The GGA results agree better with experimental data than the corresponding results calculated with the local-spin-density approximation (LSDA). In particular, the overestimation of the cohesive energies are reduced and the GGA correctly predicts the bcc ferromagnetic phase to be the ground state of Fe, while the LSDA fails to do so. We have also studied the electronic and magnetic properties of the insulating antiferromagnetic transition-metal compounds FeO, CoO, and NiO with the GGA. For these oxides it is found that the results are very similar to the results calculated with use of the LSDA.

I. INTRODUCTION

Many calculations in the past decade have demonstrated that the local-spin-density functional approximation (LSDA) gives a good description of ground-state properties of many moderately correlated systems.[1] The LSDA has become the *de facto* tool of first-principles calculations in solid-state physics, and has contributed significantly to the understanding of material properties at the microscopic level. However, there are some systematic errors which have been observed when using the LSDA, such as the overestimation of cohesive energies for almost all elemental solids, and the underestimation of lattice parameters in many cases. The LSDA also fails to give a correct prediction of the ground state of Fe.[2] For strongly correlated systems, the LSDA often fails. For example, the LSDA gives the wrong ground states for La_2CuO_4 (Refs. 3–5) and transition-metal monoxides.[6] Better exchange-correlation functional forms with gradient corrections incorporated have been suggested recently by various authors.[7–9] These new functionals have been tested recently and it is quite encouraging that the results obtained are generally better than those obtained with the LSDA. For example, the "generalized gradient approximation (GGA)" of Perdew and co-workers has yielded better results for the total energy of atoms,[7] the binding energies of the first-row diatomic molecules,[10] the ground-state properties of third-row elements,[11–13] and the cohesive properties of Al, C, and Si.[14] The purpose of the present paper is to further test the GGA by evaluating the ground-state properties of some transition metals and their monoxides. To this end we have used the GGA with a first-principles linear-combination-of-atomic-orbitals (LCAO) method to study the lattice parameters, the bulk moduli, the cohesive energies, and the magnetization of Fe, Co, and Ni. We have also studied the electronic and magnetic properties of their monoxides. We will show that the GGA gives better ground-state properties of the $3d$ elements considered than does the LSDA, but still does not give the correct ground states for the monoxides.

II. METHOD

The self-consistent calculations were performed with an accurate first-principles LCAO method.[15] The radial part of the atomic basis functions, potentials, charge densities, and spin densities are expanded about atomic sites in a series of Gaussian functions, so that most integrations and the gradient of the charge and spin density (needed for the gradient correction) are handled analytically. For the spin-dependent local-density approximation to the exchange-correction potential, we have used the Ceperley-Alder form[16] for the LSDA calculations. Gradient corrections are implemented as prescribed by the generalized gradient approximation GGA of Perdew and co-workers.[7] Besides the core states, the atomic basis consisted of $4s$, $4p$, and $3d$ functions on Fe, Co, and Ni, and for the monoxides $2s$, $2p$, $3s$, and $3p$ functions on O sites. To include even more variational freedom, we also included the $5s$ and $5p$ functions on the transition-metal atoms when we studied the monoxides. The orbitals have been obtained from converged self-consistent atomic calculations. In both the LDSA and GGA calculations in bulk environments, we use the same radial functions (composed of Gaussians) from converged self-consistent atomic calculations performed with the LSDA. This means that we neglect the relaxation of the core charge densities when we include the gradient correction in the exchange-correlation potential. We will comment on the validity of this approximation later. The self-consistent charge densities were evaluated on a uniform sampling of 112, 110, 45, 84, 280, and 30 irreducible k points for the bcc Fe, fcc Fe, antiferromagnetic (AFM) fcc Fe, hcp Co, fcc Ni, and the monoxides in the rhombohedral phase, respectively. The energy of each eigenvalue was broadened by 2 mRy so that the **k**-space summation near the Fermi level would converge more quickly.

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The total energies of the systems (Fe in the bcc and fcc phase, Co in the hcp phase with c/a equal to 1.622, and Ni in the fcc phase) are calculated as a function of volume. The results are then fitted to universal binding curves[17] which give the lattice parameters, bulk moduli, and total energies at equilibrium. The cohesive energies are then calculated by subtracting off the zero-point energies of the solids and the reference energies of the isolated spin-polarized atoms in their ground-state configurations. For the monoxides we are primarily interested to see if GGA gives the correct magnetization and band gaps. To this end, we have calculated the electronic structure for the monoxoides with the lattice parameters listed in Table I of Ref. 18. All the calculations reported here are fully self consistent. In the atomic calculations, the radial part of the wave functions, potentials, charge, and spin densities are also expanded in Gaussian functions, so as to achieve the best cancelation of errors due to basis incompleteness in the determination of cohesive energies.

III. RESULTS

A. Fe, Co, and Ni

It has been known for some time that while the LSDA gives the correct ground state for most elemental solids, it fails to do so for Fe. For this reason, it is of interest to compare GGA results with LSDA results for the structural energies of Fe and its neighbors Co and Ni. The total energies per atom for various phases of Fe are calculated as a function of volume and fitted to "universal binding curves." They are plotted in Fig. 1. The GGA results are shown as solid lines while the LSDA results are shown as dotted lines. In the figure, we have used the minimum energy for the ferromagnetic bcc (F bcc) phase as the reference energy for both the GGA and LSDA results. From the fits to the universal binding curves, we determine the Wigner-Seitz radii, bulk moduli, and cohesive energies for various phases, and they are listed in Table I. It should be mentioned that the experimental magnetic moment in Table I includes the orbital contribution, while the calculated magnetic moment does not. We find that for the fcc structure, the paramagnetic, ferromagnetic, and antiferromagnetic phases are almost degenerate in energy within the LSDA with volumes up to 78.6 a.u., and hence only the energy versus volume curve for the paramagnetic phase is shown in the figure. For the GGA results, the paramagnetic fcc and ferromagnetic fcc phases are also nearly degenerate up to 78.6 a.u., and only the curve for the paramagnetic phase is shown. Unlike the LSDA results however, the antifer-

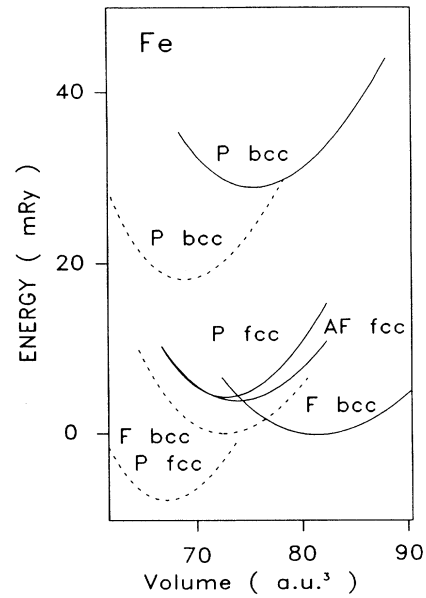

FIG. 1. Total energy of paramagnetic (P) bcc and fcc, ferromagnetic (F) bcc, and antiferromagnetic (AF) fcc Fe as a function of volume. The solid curves correspond to the GGA and dotted curves correspond to the LSDA. The curves are displaced in energy so that the minimum for the F bcc curves coincide, and this reference energy is labeled as zero.

TABLE I. Ground-state properties of Fe, Co, and Ni calculated with the LSDA and the GGA, compared with experimental values. All experimental values are quoted from Ref. 23.

		Wigner-Seitz radius (a.u.)	Bulk modulus (Mbar)	Cohesive energy (eV)	Magnetic moment (μ_B)	
Fe	LSDA	2.59	2.64	7.32	2.08[a]	2.14[b]
	GGA	2.68	1.74	6.31	2.20	2.17
	Expt.	2.67	1.68	4.28	2.22	
Co	LSDA	2.54	2.68	5.98	1.50	1.62
	GGA	2.63	2.14	4.52	1.63	1.63
	Expt.	2.62	1.91	4.39	1.72	
Ni	LSDA	2.53	2.50	5.45	0.59	0.61
	GGA	2.63	2.08	4.18	0.65	0.63
	Expt.	2.60	1.86	4.44	0.61	

[a]Magnetic moment calculated at calculated equilibrium lattice parameter.
[b]Magnetic moment calculated at the experimental parameters.

romagnetic phase in the fcc structure, consisting of alternating layers of up and down spins normal to the [001] direction, becomes lower in energy for volumes exceeding about 72 a.u. We see from Fig. 1, in agreement with previous results, that the LSDA gives erroneously the paramagnetic fcc phase as the ground state of Fe. However, the ferromagnetic (FM) bcc phase is correctly predicted to be the ground state by GGA, which is also consistent with the results of recent linear muffin-tin orbital (LMTO) and linear augmented-plane-wave method (LAPW) calculations.[11–13] The GGA Wigner-Seitz radius, the cohesive energy, and the bulk modulus agree better with experimental values than the results calculated with LSDA. There are small increases of the magnetic moment using the GGA, which is consistent with the previous LMTO calculations. The structural and magnetic properties for Co and Ni are also calculated with both the LSDA and GGA, and they are shown in Table I. For Co and Ni, the LSDA predicts the correct ground state. Nevertheless, results calculated with the GGA are in better agreement with experiments. We observe from Table I that the GGA consistently gives softer lattices (larger lattice constants and smaller bulk moduli) for the elements we have considered here. This can be rationalized in the following way. The GGA is formulated so that exchange energy is lower (more negative) than that of the LSDA, while the correlation energy is higher. Since the exchange energy is the dominant term, the gradient correction in the GGA makes the exchange-correlation energy lower than the LSDA for the same charge density. We further notice that the self-consistent charge densities obtained using the GGA is very similar to those obtained with the LSDA. So, we expect that each point on the energy versus volume curve is lowered by taking the gradient correction into account. This lowering in energy is not uniform though. For the same material, we found that that there is in general a higher charge-density gradient (and lower charge density) at larger volumes, so that gradient correction terms lower the energy of the system at larger volumes more than smaller volumes. This leads to a larger equilibrium volume and smaller bulk modulus. The larger equilibrium volumes obtained by the GGA also partly explain the slightly larger moments obtained with the GGA, since larger volumes usually favor stronger magnetization. We note that while our LSDA and GGA results have the same trend and the same relative energy ordering of various phases of Fe as the LMTO (Ref. 11) and LAPW (Ref. 12) results, there are some discrepancies in the value of the energy differences among the three calculations, which are possibly caused by different basis and **k**-point convergences in different techniques.

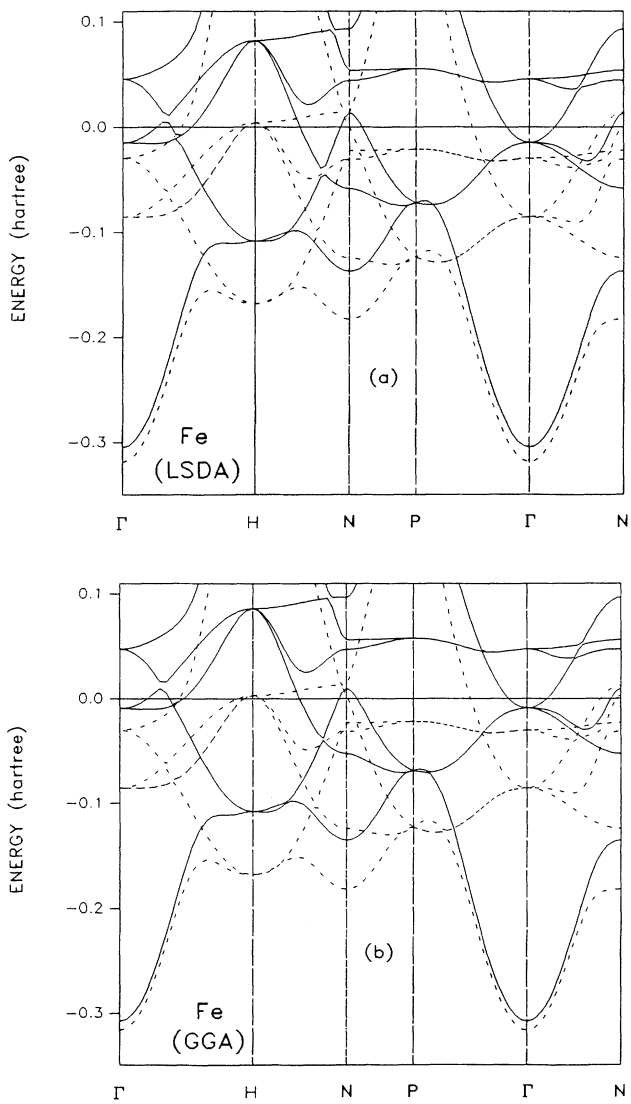

FIG. 2. Band structures for bcc Fe calculated with (a) the LSDA and (b) the GGA at the experimental lattice parameter. The solid curves are the minority spin bands while the dotted curves are the majority spin bands. The Fermi level $E_F=0$ is marked by a horizontal line.

To test the validity of neglecting the changes in the core change, we studied the Fe bcc phase in the GGA with orbitals calculated from a converged self-consistent atomic calculation using the GGA. The lattice parameter is found to be 5.47 a.u., and the bulk modulus is found to be 1.76 Mbar, compared with the values 5.46 a.u. and 1.74 Mbar calculated by neglecting the relaxation of the core charge. It is therefore a reasonable approximation.

Self-consistent LSDA and GGA band structures at the experimental lattice parameter of ferromagnetic Fe are shown in Fig. 2. The LSDA bands agree with numerous others reported.[12,19] There are only slight differences between the LSDA bands and the GGA bands, caused mainly by the slightly different moments between them.

B. FeO, CoO, and NiO

We find an antiferromagnetic ground state for FeO, CoO, and NiO at the experimental lattice parameter for both the LSDA and the GGA. The magnetic moments are found to be $3.63\mu_B$, $2.36\mu_B$, and $1.03\mu_B$ for FeO, CoO, and NiO in the LSDA, respectively, and the corresponding magnetic moments in the GGA are found to be

TABLE II. The LSDA, GGA, and experimental magnetic moments (in units of μ_B) for FeO, CoO, and NiO.

	Magnetic moment		
	LSDA	GGA	Expt.
FeO	3.63	3.55	3.32[a]
CoO	2.36	2.37	3.80[a]
NiO	1.03	1.01	1.90[b]

[a]Reference 24.
[b]Reference 25.

$3.55\mu_B$, $2.37\mu_B$, and $1.01\mu_B$. These theoretical values are compared with experimental data in Table II. We observe from Table II that the spin magnetic moments from the LSDA for these monoxides do not agree well with experiments, and the GGA results provide little or no improvement at all. Self-consistent LSDA and GGA band structures at the experimental lattice constant of antiferromagnetic FeO, CoO, and NiO are plotted in Figs. 3–5, where LSDA and GGA bands are shown in solid and dotted lines, respectively. The Brillouin zone structure and symmetry point notations can be found in Ref. 6. We find the band structures calculated by the GGA are very similar to the results calculated by the LSDA. It is a well-known problem of the LSDA that it predicts metallic ground states for many insulating $3d$ metal monoxides, and it is clear from Figs. 3–5 that the GGA does not change the picture provided by the LSDA. There are no gap openings at the Fermi level for FeO and CoO. While it is well known for insulators that density-functional calculations yield a band gap smaller than the minimum energy required to produce electron-hole quasiparticles,[20] it is disappointing when such calculations, even using the GGA, are unable to even obtain an insulating state for FeO and CoO. The band-gap problem may not be a deficiency of the generalized gradient approximation, since even the exact density functional may not give a correct band gap for these oxides.[21]

Although the GGA does not solve the band-gap problem of the transition-metal monoxides, it does give a better lattice parameter. We calculated the total energies of NiO for different lattice constants. The lattice parameter is found to be 7.98 a.u., compared with 7.73 a.u. in LSDA and 7.93 a.u. experimentally.

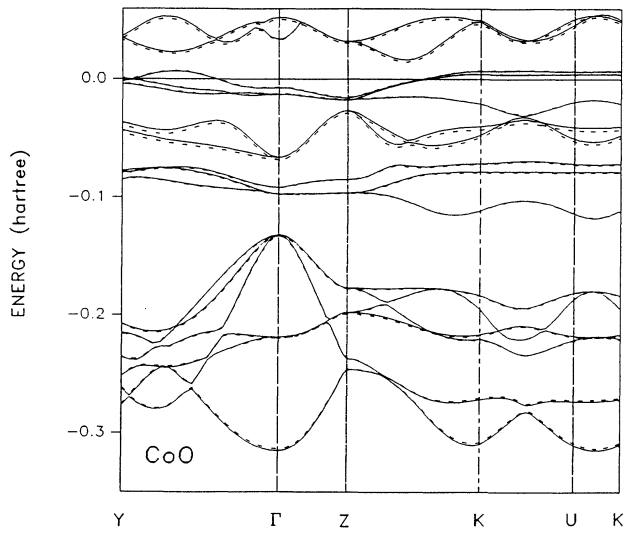

FIG. 4. Band structure for CoO at the experimental lattice parameter. The solids curves are the LSDA band while the dotted curves are the GGA bands. The Fermi level $E_F=0$ is marked by a horizontal line.

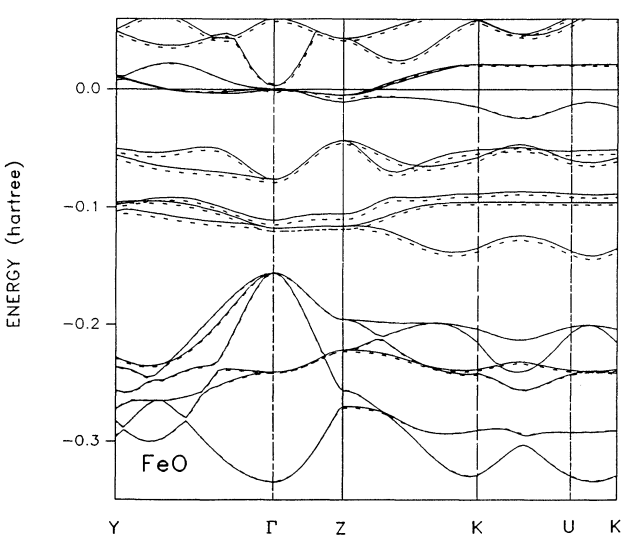

FIG. 3. Band structures for FeO at the experimental lattice parameter. The solid curves are the LSDA bands while the dotted curves are the GGA bands. The Fermi level $E_F=0$ is marked by a horizontal line.

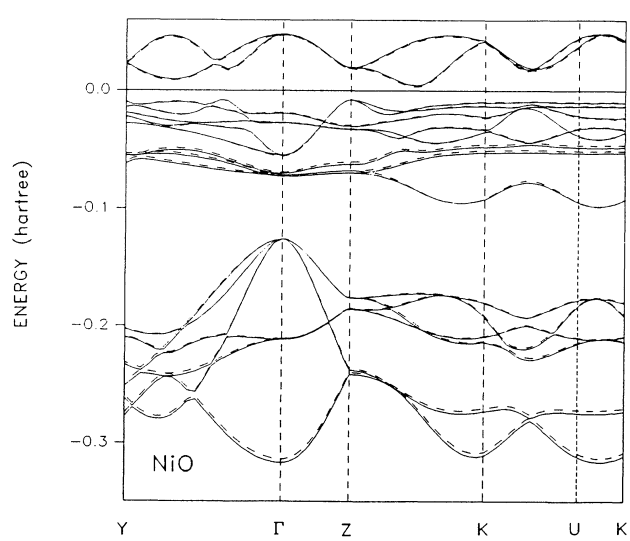

FIG. 5. Band structures for NiO at the experimental lattice parameter. The solids curves are the LSDA band while the dotted curves are the GGA bands. The Fermi level $E_F=0$ is marked by a horizontal line.

IV. CONCLUSIONS

We have shown that the LCAO method with the use of the GGA gives better ground-state properties for Fe, Co, and Ni. In particular, the ground state of Fe is predicted correctly by GGA to be ferromagnetic bcc, while LSDA fails by predicting it to be fcc. On the other hand, the GGA does not solve the problem encountered in the transition-metal monoxides. The magnetic moments and band structures obtained with the GGA for the oxides are essentially the same incorrect ones as obtained with the LSDA.

The inclusion of the GGA gradient corrections in our LCAO code is easy to implement, and only a little extra CPU time is required to calculate the GGA potential. In view of the ease of implementation, the use of the GGA thus seems warranted for most calculations of ground-state properties of solids. However, we should note that the GGA is not a panacea. While it improves on LSDA results for many cases as far as structural and cohesive properties are concerned, it offers like improvement for the magnetic moments of some insulating $3d$ metal monoxides. To obtain the correct insulating ground states for these strongly localized and correlated systems, other methods such as the self-interaction corrections[22] may be needed.

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