Theory of Magnetic and Structural Ordering in Iron

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Using the total-energy general-potential linearized-augmented-plane-wave method, we have tested the adequacy of the local-spin-density approximation for describing the magnetic and structural properties of iron. We find that there are fundamental deficiencies in the local-spin-density approximation, both quantitative and qualitative, in that there are substantial errors in the calculated ground-state volumes and magnetic moments, as well as a prediction of the wrong ground-state crystal structure.

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It has recently been established that the local-spin-density approximation (LSDA) within the density-functional theory can provide an accurate theoretical estimate of static structural properties, phonon spectra, crystal stability, and pressure-induced phase transformations in solids. These achievements are important because they establish a new approach for predicting, from first principles, the structural properties of more complicated systems where theoretical understanding has been limited to empirical methods and experimental data may be lacking. However, the limitations of the LSDA for magnetic materials, such as iron, are still open to question. In this Letter we assess the accuracy of the LSDA in describing the magnetic and structural ordering in $3d$ transition metals, based on total-energy calculations for fcc and bcc iron as a function of volume and type of magnetic order.

A comprehensive study of the ground-state properties of metals, including $3d$ ferromagnetic metals, has been reported by Moruzzi, Janak, and Williams[1] using the Korringa-Kohn-Rostoker (KKR) method with a LSDA exchange-correlation potential. Kübler[2] subsequently used the augmented-spherical-wave (ASW) method to calculate the total energies of nonmagnetic (NM), ferromagnetic (FM), and antiferromagnetic (AFM) states for both bcc and fcc phases of iron for a range of atomic volumes near equilibrium. The FM state was found to have the lowest energy in the bcc case while the AFM state is the lowest in the fcc case. Surprisingly, the latter was calculated by Kübler to lie 1184 K lower in energy than the former, which is the actual observed ground state of iron at zero temperature. The muffin-tin (MT) approximation, used in the ASW calculations, was suspected to be the most likely cause of the discrepancy.

To investigate this point further, use has been made of a self-consistent linearized-augmented-plane-wave (LAPW) method[3] which is free from any shape approximations to the potential and charge density. The method has been tested and found to work well on a variety of different systems. Specifically, we have studied the NM and FM phases of both bcc and fcc iron, as well as an AFM fcc phase which consists of alternating layers of up and down spins normal to the [001] direction. What is done for the first time here is to obtain a more accurate estimate of the crystal structure difference in the total energy of iron which, in the past, has been limited by the use of the MT approximation.

We have found the fcc phase more favorable among the two NM states, which is consistent with the fact that Ru, the $4d$ counterpart of Fe, is hcp. In the bcc case our results give the normal FM state as 3334 K lower in energy, 6.7% larger in equilibrium volume, and 15% smaller in bulk modulus than the NM bcc state. In the fcc case, we find two metastable FM states, with the ground state being either AFM or NM (the two are degenerate within our numerical accuracy). Most notably, the AFM or NM fcc phase has the lowest energy (867 K lower in energy than the FM bcc phase). We believe the failure to predict the proper ground state of iron indicates a fundamental difficulty in the LSDA for describing the magnetic interaction in $3d$ transition metals.

Before discussing our results further, we summarize the salient points regarding the theoretical and numerical approaches we have used. The LAPW calculations closely follow the methods discussed in Ref. 3 with the

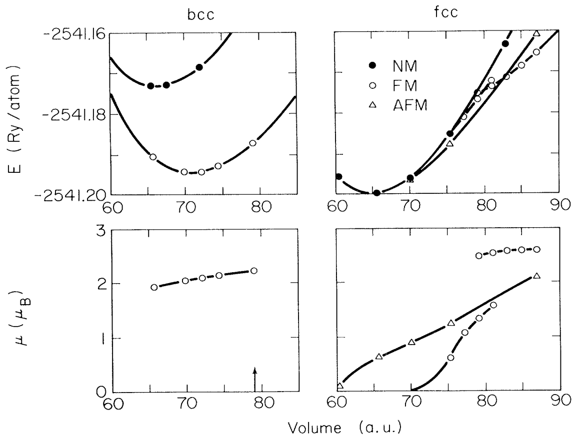

FIG. 1. Total energy per atom (E) and magnetic moment (μ) of nonmagnetic (NM), ferromagnetic (FM), and antiferromagnetic (AFM) states of bcc and fcc iron.

iron-core states treated self-consistently with use of the full Dirac equation for the spherical part of the potential and the valence electrons treated in the semirelativistic approximation which neglects spin-orbit coupling. The self-consistent charge densities were evaluated by a histogram sampling of 40, 60, and 30 special **k** points in the irreducible Brillouin zone for the bcc, fcc, and AFM fcc phases, respectively, with an artificial temperature broadening of 2 mRy. All nonspherical and non-MT corrections to the charge density and potential were explicitly included in the self-consistent iterations. Careful tests of the sensitivity of the total energy to basis set size and to the choice of the LAPW energy parameters were performed. Overall, the structure differences of our total energies have an absolute error of less than 1 mRy.

For the LSDA exchange-correlation potential we used the parametrization of Vosko and co-workers[4] which is generally believed to be the most vigorous and accurate. This potential interpolates between the well known high- and low-density limits, using the exact Monte Carlo calculations of Ceperley and Alder[5] at intermediate densities for both the NM and completely polarized electron gases. For intermediate spin polarization, however, the spin-dependent part of the potential is scaled according to the random-phase approximation.

The total energy per atom calculated for the bcc and fcc phases is shown in Fig. 1 together with the atomic moments. The solid lines are obtained from least-squares fits to the Murnaghan equation of state[6] from which one can determine the equilibrium lattice constants and bulk moduli. They are given in Table I. For FM bcc iron, our calculated equilibrium lattice constant, 5.212 a.u., and bulk modulus, 2.66 Mbar, are in good agreement with recent independent calculations of Hathaway, Jansen, and Freeman.[7] The corresponding experimental values are 5.406 a.u. and 1.68 Mbar, respectively. The discrepancy between theory and experiment is larger than what is typically found for nonmagnetic materials.

The band theory of ferromagnetism is now well understood. The magnetic interaction leads to a spin splitting of the *d* bands and a filling of the less bonding majority-spin orbitals at the expense of the more bonding minority-spin orbitals. This causes the volume to increase, which in turn reduces the compression the *sp* electron feel (i.e., reduces their kinetic energy), and hence the bulk modulus. Ferromagnetism is established if the Stoner criterion is realized. The NM density of states at the Fermi energy must be reasonably high so that the gain in the kinetic energy is more than compensated for by the loss in the exchange energy. The above conditions are satisfied in the bcc phase. We found that ferromagnetism lowered the total energy by 3334 K, accompanied by an expansion in volume (6.7%) and a reduction in the bulk modulus (15%). This energy difference should not be confused with the Curie temperature ($T_C = 1041$ K) which is the temperature above which the *average* magnetization vanishes. Over this temperature range the thermodynamics is dominated by spin-wave-like excitations (changes in the direction of

TABLE I. Total energy per atom (E) at equilibrium lattice constant (a), bulk modulus (B), and atomic magnetic moment (μ) of NM, FM, and AFM states of bcc and fcc Fe.

		E	a (a.u.)	B (Mbar)	μ (μ_B)
bcc	NM	−2541.173	5.10	3.14	· · ·
	FM	−2541.194	5.21	2.66	2.08
fcc	NM	−2541.200	6.38	3.44	· · ·
	AFM	−2541.200	6.38	3.23	0.64
	FM$_1$	−2541.200	6.37	3.90	0.00
	FM$_2$[a]	−2541.175	6.81	· · ·	2.47

[a]There is no equilibrium solution for the high-spin state of fcc FM$_2$ iron in the sense that there is no volume for which the pressure vanishes.

the exchange fields) rather than Stoner-type excitations (changes in the magnitudes of the exchange fields).[8] Thus, substantial local moments persist even above T_C in contrast to the NM states that we have considered. This is supported by many experiments including the exchange splitting close to T_C observed in photoemission.[9]

At normal pressure, experiment indicates that the bcc phase of iron is stable below 1183 K (α phase) and above 1663 K, up to the melting point of 1807 K (δ phase). Between 1183 and 1663 K, the fcc γ phase is stable but the temperature is too high for long-range magnetic ordering to occur. Therefore, the magnetic properties of γ-Fe at low temperatures are not well understood.

Early measurements on the fcc Fe alloys,[10] and small particles of fcc-Fe precipitates from supersaturated Cu-Fe solid solutions,[11] led to the conclusion that the ground state of fcc iron is AFM. However, more recent measurements of small-particle precipitates from Cu-Au alloys indicate FM.[12] In addition, films of fcc iron grown on copper surfaces may be either FM or AFM, depending on the crystallographic surface on which the growth occurs.[13] Recent neutron measurements on bulk γ-Fe at high temperature indicate the presence of FM correlations and a substantial local moment.[14]

At normal pressure our results shown in Fig. 1 indicate that the NM and AFM phases of fcc Fe are essentially degenerate. This near-degeneracy is consistent with the low Néel temperature observed in fcc Fe alloys, but is in contrast to Kübler's calculation which placed AFM fcc Fe 1183 K lower in energy than NM fcc Fe. Our results are supported by the fact that our calculations show that the total energy of AFM fcc Fe converges to that of the NM fcc Fe when the atomic moment vanishes. Unlike the FM-NM transition in bcc Fe, there is very little change in the equilibrium volume and bulk modulus between AFM and NM states of the fcc iron. This may be due in part to the small atomic moments ($0.64\mu_B$) in the AFM fcc Fe compared to that of the FM bcc Fe ($2.08\mu_B$). The small differences in the atomic moments from previous calculations[1,2,15-17] may reflect (1) different lattice constants, (2) different choices of exchange-correlation potentials, (3) semirelativistic effects which tend to lower the *sp* states relative to the *d* bands, and (4) the use of the MT approximation in some cases.

In good agreement with earlier calculations,[2,16] our total energy as a function of atomic volume for FM fcc Fe exhibits two local minima, with the magnetic moment increasing abruptly between them. Thus, our results support the idea the FM fcc Fe can exist in two states with only slightly different energies: a low-volume, low-spin, large–bulk-modulus state, and a high-volume, high-spin, small–bulk-modulus state. The coexistence of two spin states in FM fcc Fe has long been postulated to explain the Invar anomalies. The origins of the two spin states has been discussed in terms of features of the density of states,[16,18] while Bagayoko and Callaway[15] have identified the abrupt transition with the occupancy of a nearly flat portion of the *d* bands and the disappearance of the corresponding Fermi surface.

Our results can also resolve a small discrepancy regarding the transition from the low-spin state to the high-spin state: Kübler[2] found the transition between $r_s = 2.64$ and 2.65 a.u. and a moment of $1\mu_B$ while Bagayoko and Callaway[15] reported a larger value of $r_s(2.71)$ and moment ($1.52\mu_B$). We found metastable solutions for *both* high- and low-spin states between $r_s = 2.66$ and 2.68 a.u. In the low-spin phase, the corresponding atomic moments increase sharply from $1.35\mu_B$ to $1.56\mu_B$. The possibility of more than one solution in a self-consistent calculation was first discovered by Janak[19] in ferromagnetic cobalt.

As can be seen in Fig. 1, the atomic moment decreases with decreasing volume, which indicates that there is a transition back to the NM state as the volume shrinks, the band width increases, and the electrons become delocalized. On the high-volume side, there is another transition in fcc Fe from AFM to the high-spin state of FM near $r_s = 2.69$ a.u. This is consistent with the experimental observations that fcc-Fe precipitates in Cu ($r_s = 2.67$) are AFM[11] and fcc-Fe precipitates in Cu-Au alloys ($r_s = 2.78$) are FM.[12]

The major result of the present study is that both NM and AFM fcc Fe lie lower in energy than does FM bcc Fe by 867 K. This emphasizes a shortcoming of LSDA in incorrectly describing the effect of the Hund's-rule correlations that are responsible for the formation of atomiclike local moments. Within LSDA, the exchange and correlation potentials are determined *locally* on the basis of the results of a *homogeneous* electron gas of the same spin density at that point. The determination of these local potentials makes no distinction as to whether the spins of the nearest-neighbor atoms are parallel or antiparallel and, therefore, some of the correlations between local moments on different sites are neglected. It is possible that the $3d$ electrons in iron are localized enough for this effect to become important. Recently, one of us[20] has studied the effects of a nonlocal exchange potential and found a sizable correction to the exchange splitting in nickel. Similar attempts in iron, however, failed because the correction is again large in spite of the good agreement between the uncorrected LSDA energy bands and experiments. These results may be an indication of substantial cancellation between nonlocal exchange and nonlocal correlation corrections, which must be treated on an equal footing. Hopefully, the present Letter will stimulate more work along these directions.

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