Lattice-parameter dependence of ferromagnetism in bcc and fcc iron

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A series of self-consistent-band calculations have been performed for a ferromagnetic state of iron in both the bcc and fcc structures. The dependence of the magnetic moment per atom on the lattice parameter was obtained. The linear combination of Gaussian orbitals method was employed in conjunction with a local-density exchange-correlation potential. An explanation is given for the abrupt increase in the magnetic moment in the fcc case near $r_s = 2.7$ in terms of behavior of the band structure.

I. INTRODUCTION

The electronic properties of metallic iron have been of interest for many years. Energy-band calculations prior to 1973 are listed by Tawil and Callaway.[1] Recent reviews are presented in Refs. 2–4.

In contrast to the case of nickel, there is general agreement between recent calculations[5,6] and experimental measurements of band-structure and Fermi-surface properties.[2] Most of the calculations and experiments pertain to the body-centered-cubic phase, which is the most stable one under normal conditions of temperature and pressure (lattice constant 5.4057 a.u. at $T=0$).

The properties of fcc iron, which is the stable phase in a temperature region above the Curie temperature, are less understood. Small particles of fcc iron can be obtained as precipitates from supersaturated Cu-Fe solid solutions. These are antiferromagnetic.[7–9] Ferromagnetic particles are obtained as precipitates from Cu-Au alloys.[10] Films of fcc iron grown on copper surfaces may be either ferromagnetic or antiferromagnetic, depending on the crystallographic surface on which the growth occurs.[11–13] Recent neutron-diffraction measurements on bulk fcc iron at high temperatures indicate the presence of ferromagnetic correlations and a substantial local moment.[14]

This note reports results of self-consistent calculations of the band structures of both bcc and fcc ferromagnetic iron over a fairly wide range of lattice parameters. The calculations are made using the local-density approximation to density-functional theory.

Similar calculations have been performed by Andersen and co-workers,[15–17] who used the canonical band method, and by Kubler.[18] Kubler's work is closely related to ours, and we shall discuss it below.

Kubler employed the "augmented-spherical-wave" (ASW) procedure[19] and a potential obtained from density-functional theory to calculate the total energies of nonmagnetic, antiferromagnetic, and ferromagnetic states of both bcc and fcc phases of iron for a range of atomic volumes close to equilibrium. In the bcc case the normal ferromagnetic state was found to have the lowest energy. The magnetic moment per atom in this state was found to be a smoothly increasing function of atomic volume. In contrast, for the fcc crystal the antiferromagnetic structure was found to have the lowest energy, and indeed had a lower energy than that of the bcc ferromagnet. The magnetic moment of the fcc ferromagnet was found to increase quite abruptly from a low value less than $1\mu_B$ per atom to a high value (greater than $2\mu_B$ per atom) as the radius of the Wigner-Seitz sphere r_s increased from 2.64 to 2.65 a.u. This transition was first described theoretically by Madsen and Andersen.[15] This supports the idea that fcc iron can exist in two states, whose energies are only slightly different: a low-volume, low-spin state and a high-volume, high-spin state.[20–22]

We report here the results of similar calculations. Our work is more limited in some extents than that of Kubler in that we consider the ferromagnetic state only, for both bcc and fcc iron, and do not calculate total energies, but we perform full band calculations. Our calculational methods and our results are discussed below.

II. COMPUTATIONS

We have used the linear combination of Gaussian orbitals (LCGO) method[23] with a local-density potential of

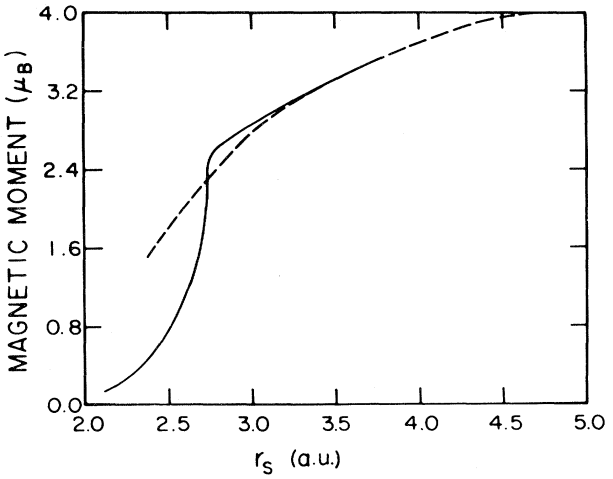

FIG. 1. Magnetic moment per atom in fcc (solid line) and bcc (dashed line) iron is shown as a function of the Wigner-Seitz sphere radius.

TABLE I. Density of states (states/atom Ry) for majority- (up-) and minority- (down-) spin electrons at the Fermi energy [(Ry atom)$^{-1}$], magnetic moment (μ_B per atom), and characteristic exchange splitting Δ_c (Ry) for bcc and fcc ferromagnetic iron.

	bcc				fcc				
r_s	$N_\uparrow(E_F)$	$N_\downarrow(E_F)$	μ	Δ_c	r_s	$N_\uparrow(E_F)$	$N_\downarrow(E_F)$	μ	Δ_c
2.462	8.321	6.736	1.735	0.142	2.112	5.219	5.206	0.126	0.017
2.560	9.263	3.892	1.987	0.162	2.188	5.985	5.832	0.186	0.042
2.661	11.036	3.341	2.153	0.172	2.345	7.639	9.140	0.397	0.057
2.757	13.906	4.802	2.317	0.177	2.560	12.068	10.097	0.966	0.090
2.954	2.582	19.649	2.717	0.197	2.661	23.826	10.330	1.517	0.120
3.447	2.923	60.269	3.269	0.232	2.736	2.470	13.346	2.549	0.187
4.431	1.106	484.124	3.943	0.277	3.517	2.739	36.140	3.359	0.215

standard form[24] to compute band structures of ferromagnetic bcc and fcc iron over a range of Wigner-Seitz sphere radii between 2 and 5 a.u. These calculations are fully self-consistent. However, in order to reduce the amount of computer time required for these computations, the basis set of independent Gaussians used in previous work[5] was reduced by contraction, as described elsewhere.[25]

Specifically, we have used a basis of 43 partially contracted Gaussian-type orbitals GTO's (eight s-type functions, five p-type, and four d-type) in contrast to the 75 independent GTO's used in Ref. 5. The calculations were considered to have achieved a satisfactory degree of self-consistency when the change in all the Fourier coefficients of the Coulomb potential was less than 10^{-4} Ry for two consecutive iterations. Subsequently, the band structure was calculated at 505 and 506 points of the irreducible wedge for fcc and bcc structures, respectively. In the case of the bcc structure at the normal lattice spacing, for which detailed comparison of calculations is possible, the present results and those of Ref. 5 are in very substantial agreement, indicating that the effect of the use of contractions is quite mild, except for a nearly rigid shift of the bands to higher energy as discussed elsewhere.[25] In particular, we find a magnetic moment of $2.15\mu_B$/atom, which is 0.01 smaller than given in Ref. 5; the exchange splitting of P_4 is smaller by 0.03 eV, and the majority-spin d-band width (at P) is about 0.1 eV smaller. Some portion of these small differences may be due to the use of an improved parametrization of the exchange-correlation potential.[24] Our previous experience in the case of nickel[4] indicates such changes are quite small. The calculated charge and spin form factors are essentially unchanged. Although only ferromagnetic ordering was considered, we have observed previously in other systems[26] that if the nonmagnetic state has a lower total energy than that of the ferromagnetic state, if the iterative cycle leading to self-consistency is started with the assumption of a nonzero moment, it will be reduced to zero in a few iterations. Thus we think it is likely, although we have not demonstrated it explicitly, that the total energy of the ferromagnetic state is lower than that of the nonmagnetic state for all the values of the lattice parameter considered here. We are, of course, unable to comment on that of an antiferromagnetic state.

III. RESULTS AND DISCUSSION

The magnetic moment per atom as calculated for the bcc and fcc phases are shown as a function of r_s, the radius of the Wigner-Seitz sphere, in Fig. 1. Some representative numerical values are given in Table I for this quantity, the density of states at the Fermi energy, and for a characteristic exchange splitting as determined by the separation of major peaks in the up- and down-spin density of states. Additional numerical results characterizing the band structure are presented in Tables II and III, in which we give the d- and s-p—band widths and the exchange splitting of some states of high symmetry for several lattice parameters. These data can be interpreted qualitatively as showing a gradual tendency toward localization of the d electrons in that the width of the exchange-split subbands becomes small compared to the exchange splitting itself. Additional results and details of this calculation can be found in Ref. 27.

TABLE II. Representative band widths and exchange splittings for bcc iron (in Ry) for various atomic radii or lattice constants (in a.u.).

r_s	a	$W_{sp\downarrow}$ ($H_{15\downarrow}$-$\Gamma_{1\downarrow}$)	$W_{d\uparrow}$ ($P_{3\uparrow}$-$P_{4\uparrow}$)	$W_{d\downarrow}$ ($P_{3\downarrow}$-$P_{4\downarrow}$)	$W_{d(\uparrow\downarrow)}$ ($P_{3\downarrow}$-$P_{4\uparrow}$)	$\delta E_{ex}(\Gamma_1)$	$\delta E_{ex}(N_1)$	$\delta E_{ex}(P_4)$	$\delta E_{ex}(P_3)$
2.4619	5.0	1.5533	0.2579	0.3262	0.4017	0.0176	0.0691	0.0755	0.1438
2.5603	5.2	1.4326	0.2166	0.2913	0.3798	0.0159	0.0794	0.0885	0.1632
2.6616	5.4057	1.3211	0.1822	0.2579	0.3540	0.0150	0.0855	0.0961	0.1718
2.7573	5.6	1.2269	0.1557	0.2310	0.3349	0.0147	0.0916	0.1039	0.1793
2.9542	6.0	1.0626	0.1114	0.1857	0.3094	0.0157	0.1079	0.1237	0.1980
3.4466	7.0	0.7742	0.0425	0.1141	0.2758	0.0212	0.1417	0.1617	0.2332
4.4313	9.0	0.3808	0.0062	0.0617	0.2792	0.0533	0.1881	0.2176	0.2534

TABLE III. Representative band widths and exchange splittings for fcc iron (in Ry) for various atomic radii or lattice constants (in a.u.).

r_s	a	$W_{sp\downarrow}$ $(X_{4'\downarrow}\text{-}\Gamma_{1\downarrow})$	$W_{d\uparrow}$ $(X_{2\uparrow}\text{-}X_{3\uparrow})$	$W_{d\downarrow}$ $(X_{2\downarrow}\text{-}X_{3\downarrow})$	$W_{d(\uparrow\downarrow)}$ $(X_{2\downarrow}\text{-}X_{3\uparrow})$	$\delta E_{ex}(X_3)$	$\delta E_{ex}(X_2)$	$\delta E_{ex}(\Gamma_{25'})$	$\delta E_{ex}(\Gamma_{12})$
2.1125	5.4057	1.3111	0.8316	0.8537	0.8631	0.0094	0.0314	0.0224	0.0266
2.1885	5.6	1.2158	0.7164	0.7410	0.7552	0.0141	0.0388	0.0286	0.0338
2.3448	6.0	1.0479	0.5302	0.5603	0.5886	0.0283	0.0584	0.0449	0.0530
2.5603	6.5516	0.8695	0.3532	0.3928	0.4508	0.0580	0.0976	0.0771	0.0918
2.6616	6.8107	0.8026	0.2927	0.3365	0.4184	0.0818	0.1257	0.1020	0.1195
2.7356	7.0	0.7602	0.2544	0.3080	0.4443	0.1362	0.1899	0.1639	0.1814
3.5172	9.0	0.4858	0.0365	0.0503	0.2680	0.2177	0.2315	0.2221	0.2278

It will be observed in Fig. 1 that for values of r_s below about 2.65 a.u. the moment per atom in the fcc structure is less than that in the bcc structure, and goes to zero rapidly as r_s decreases. An abrupt increase in the moment occurs as r_s increases from 2.66 to 2.74 a.u. A graph of the energy difference $E_F - E_{(W_{1'\uparrow})}$ leads to an estimate that the transition (see below) occurs for $r_s = 2.71$. These results are in qualitative agreement with those of Kubler, but there are two quantitative differences. We find that the transition occurs for slightly larger values of r_s (he places it between 2.64 and 2.65), and we obtain a larger moment at the onset of the rapid increase ($1.52\mu_B$/atom) than he reports (less than $1\mu_B$/atom).

For larger values of r_s, the magnetic moment is nearly the same in both structures and approaches the atomic limit ($4\mu_B$/atom) smoothly. Also, beyond about $r_s = 9$ the structure of the d bands change as t_{2g} and e_g subbands separate because the "crystal-field" splitting becomes larger than "overlap" effects. The exchange splitting of the d bands is then much larger than subband widths, and we obtain two narrow subbands, separated by about 3 eV and overlapped by a wide s-p band.

Roy and Pettifor[28] have discussed the low- and high-moment states of fcc iron in terms of features of the density of states. Here, we relate the abrupt change in the moment to specific features of the band structure. Our description of the transition identifies the physics underlying the discussion of Roy and Pettifor. The situation may be appreciated by examining the majority-spin ("up") band structure for $r_s = 2.66$ and 2.74 a.u. Graphs of these are given in Figs. 2(a) and 2(b). For $r_s = 2.66$, the majority-spin band structure in iron resembles the minority-spin band structure in nickel. In particular, there is a region of holes in the nearly flat upper d band along the face of the Brillouin zone (X_5-$W_{1'}$-L_3). The band line X_5-$W_{1'}$ would be totally flat if only nearest-neighbor interactions were considered in a tight-binding model, but a small width occurs with $W_{1'}$ higher than X_5 because of second- and higher-neighbor interactions. It is a characteristic difference between d bands in fcc and bcc lattices at normal lattice spacings that in the former the flat band region and the corresponding peak in the density of states occur at the top of the band, while in the latter, a similar phenomenon occurs but somewhat below the top. At $r_s = 2.74$, this region of holes has disappeared: This portion of the majority-spin band structure now lies below the Fermi energy, and the states are occupied. The near flatness of the bands implies that there is a substantial increase in the moment.

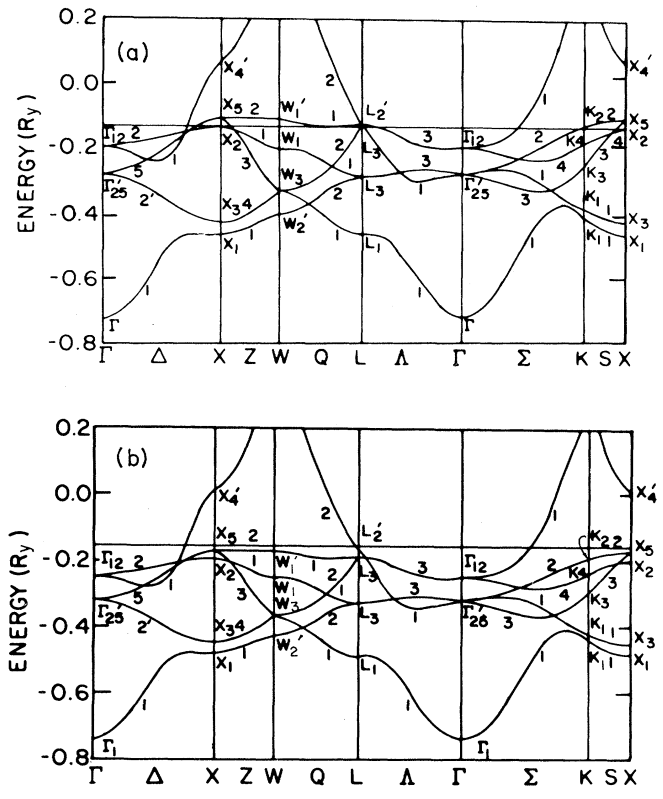

FIG. 2. (a) Band structure for majority-spin electrons in fcc iron for $r_s = 2.68$. The horizontal line indicates the Fermi energy. (b) Same for $r_s = 2.74$.

It is evident from this picture that the transition between low-moment and high-moment states is continuous, and may be considered to have occurred when E_F-$E_{(W_{1'\uparrow})}$ becomes positive. One would expect that the second derivative of the magnetization with respect to the lattice parameter would have an infinite discontinuity at the value where this band sinks below the Fermi energy.

Since the transition involves the occupancy of a nearly flat portion of the band structure and the disappearance of a part of the Fermi surface, we may regard it qualitatively

as resulting in an increasing degree of localization of the majority-spin d electrons. Above the transition, the only majority-spin d bands cutting the Fermi energy are the strongly hybridized ones (mixing s and p with d) in the neighborhood of the zone face. For such larger lattice parameters, fcc iron is a strong ferromagnet.

These results are consistent with the experiment of Gonser *et al.*[10] We assume in agreement with Kubler[18] that for atomic volumes smaller than that at which the transition to the high-moment state occurs, the antiferromagnetic state has lower energy than the ferromagnetic, while for larger volumes, the ferromagnetic state has the lower energy. It is also assumed that the atomic spacings in the Fe precipitates in both Cu and Cu-Au alloys are those given by Gonser *et al.*[10] Then the antiferromagnetic precipitates in Cu, for which $r_s=2.67$, are on the low-moment side of the transition, whereas the precipitates in Cu-Au alloys with $r_s=2.78$ on the high-moment side. Thus the experimental observations can be interpreted as implying that the transition occurs between $r_s=2.67$ and 2.78. Our estimated value is $r_s=2.71$.

IV. CONCLUSIONS

We have studied, by fully self-consistent-band calculations based on the local-density approximation to density-functional theory, the band structures of ferromagnetic fcc and bcc iron over a range of lattice parameters. A rapid increase in the moment in fcc iron occurs in the neighborhood of $r_s=2.7$ a.u., which we attribute to the occupancy of a portion of the majority-spin band structure near the surface of the Brillouin zone. These results are in qualitative agreement with those of Andersen and coworkers[15,17] and Kubler.[18] Our calculations may be more accurate quantitatively. The identification of the portions of the band structure responsible has not, to our knowledge, been reported previously.

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