Difference in total energy between bcc and fcc iron

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Motivated by discrepancies in recent calculations of the stability of bcc versus fcc iron, based on density-functional theory, we have investigated the effects of various approximations on the total energy of bcc and fcc iron. We find that in order to discuss phase stability on a 1 mRy/atom scale a careful analysis of the integrations in the Brillouin zone is necessary. A muffin-tin approximation to the shape of the potential and charge density induces errors of about 4 mRy/atom for the difference between fcc and bcc iron, and indicates that the effects of the atomic-sphere approximations must be investigated more thoroughly. Employing different approximations to the local-density form of the exchange and correlation energy yields changes in the relative values of the total energy of 2 mRy/atom, and hence this approximation also is important when total-energy differences are small.

Practical implementations of density-functional theory require some kind of approximation for the functional describing exchange and correlation (and part of the kinetic energy). At present most calculational schemes rely on a local approximation, in which the exchange-correlation energy at a given point in space depends only on the value of the charge and spin density at that same point. These calculations have shown a rather remarkable ability to reproduce experimental results in discussions of stability and phase transitions. Such discussions raise the important question of where these local approximations break down. One recent calculation for iron[1] shows that the local spin-density approximation yields the prediction that for iron the fcc phase is the most stable, in conflict with experiment. This conclusion has been contradicted, however, by other calculations[2] in which bcc ferromagnetic iron is predicted to be more stable, albeit with a very small energy difference. Resolution of these conflicting results requires discussion of the numerical precision of the computational procedures involved. These calculations differ in two ways: they use different spin-polarized forms of the local-density exchange-correlation potential, and the calculations in Ref. 2 make a sphericalization assumption not made in Ref. 1. In this Brief Report we present results of detailed calculations which explain the numerical differences, verify the results of Ref. 1, and support the conclusion that the local spin-density approximation indeed gives incorrect results when applied to iron.

Our computational procedures are basically the same as those used in Ref. 1, but the programs are developed independently. Our results[3] agree with the results given in Ref. 1 for the equilibrium lattice constant and bulk modules of bcc iron using the parametrization of Vosko, Wilk, and Nusair[4] (VWN) of the exchange and correlation potential. We obtain an absolute value of the total energy which differs by only 1 mRy/atom from Ref. 1. In this paper we use the von Barth–Hedin (vBH) form of the exchange-correlation potential as parametrized by Janak.[5] This change in the exchange-correlation potential reduces the bcc-fcc difference in the equilibrium value of the total energy from 6 ± 1 mRy/atom to 4 ± 1 mRy/atom, with fcc iron still being more stable. Hence the effect of the choice of the approximation to the exchange and correlation potential is about 2 mRy/atom and cannot be ignored in studies where one discusses phase transitions between crystal structures with energy differences of less than 1 mRy/atom for a large range of volumes.

The main problem in electronic structure calculations is the integration in reciprocal space. The convergence of any method of integration in k space is determined by the Fermi surface of the material being studied, and analytical error behavior only holds when the density of sampling points in the Brillouin zone is sufficiently large and describes the Fermi surface very well. We employ the linear tetrahedron[6] method, in which the Brillouin zone is divided into small tetrahedra. Inside each tetrahedron energy eigenvalues are linearly interpolated between the four corner points. The dominant error in this scheme is due to a misrepresentation of the Fermi surface. It is easy to show that one introduces an error proportional to the inverse fourth power of the size of a small tetrahedron for each tetrahedron which intersects the Fermi surface. An integration over the whole Brillouin zone then leads to an error proportional to the inverse square of the size of a small tetrahedron, or proportional to the number of points in the Brillouin zone to the power $-\frac{2}{3}$. This asymptotic behavior is observed in previous calculations.[7]

In Fig. 1 we plot the value of the difference in total energy from a calculation with 210 points versus the number of points in the Brillouin zone to the power $-\frac{2}{3}$, which should give a straight line in the asymptotic region. This is approximated for more than 100 points in the irreducible wedge of the Brillouin zone. Because of the thermal broadening used in the special k-point technique of Ref. 1 a slightly smaller number of points is probably needed there, although one should investigate the effect of the thermal broadening on a mRy/atom
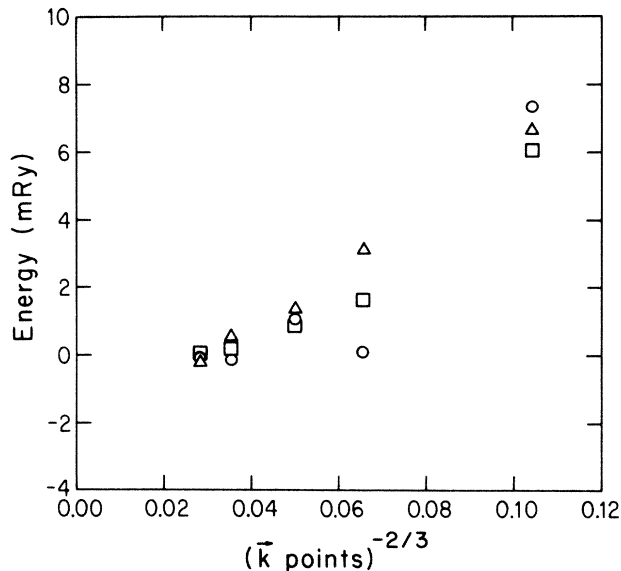
FIG. 1. Total energy (with respect to a 210-k-point calculation) as a function of the number of k points to the power $-\frac{2}{3}$ for bcc paramagnetic ($\bigcirc$), bcc ferromagnetic ($\square$), and fcc paramagnetic ($\triangle$).

TABLE I. Total energy changes for different shape approximations to the charge density and the potential. Values are in mRy/atom and give the difference with respect to a full potential calculation.

	Warped muffin tin	Muffin tin
bcc paramagnetic	1.2	9.2
bcc ferromagnetic	2.2	9.4
fcc paramagnetic	0.5	13.5

scale. From Fig. 1 we predict that our calculations for 210 k points still have absolute errors of about 2 mRy/atom. The relative errors between bcc paramagnetic, bcc ferromagnetic, and fcc paramagnetic are less than 1 mRy/atom, however, and therefore the k-space integration is not responsible for the discrepancies in total energy of fcc and bcc iron as found in Refs. 1 and 2.

Finally, we have investigated the changes in total energy due to approximations to the shape of the potential and the charge density. We defined a sphere of radius 2.25 a.u. around each iron atom, and inside these spheres we expand the potential and charge density in spherical harmonics, outside in plane waves. Each of these expansion can be truncated to the first term only. The so-called warped-muffin-tin approximation takes a spherical charge density and potential inside the spheres, while the muffin-tin approximation in addition takes a constant value of these quantities outside the spheres. The self-consistent results of these two approximations are shown in Table I, where we present the increase in total energy as compared to a full potential calculation. These values pertain to 30-k-point calculations, but they are representative for the numerical errors because at this level of convergence the errors due to different approximations are almost independent.

We see that in these highly symmetric crystal structures the nonspherical terms inside the muffin-tin sphere make only a small contribution to the total energy. This is due to the fact that the first l value which contributes is $l=4$. Relative values between bcc and fcc change by 0.7 and 1.7 mRy/atom. A much larger contribution, in the opposite direction, is due to the interstitial terms. They have a similar effect for ferromagnetic and paramagnetic bcc iron, but a much stronger effect for fcc iron. It is reassuring to find that the shape approxima-

tions to the potential and change density do not severely affect differences between paramagnetic and ferromagnetic bcc iron. Accordingly, the difference in equilibrium total energy between these two states is 23 mRy/atom in Ref. 2, 21 mRy/atom in Ref. 1, and also 21 mRy/atom in our previous work.[3] Therefore, we only compare our bcc results with paramagnetic fcc iron, because we expect that the differences between paramagnetic and ferromagnetic fcc iron will be very similar to the results of Ref. 1. These conclusions are, of course, not general and are only valid here because the interstitial charge density in iron is mainly due to the s-p electrons, which are only slightly antipolarized in the magnetic phases.

The interstitial charge densities in bcc and fcc iron are different due to the change in local environment (8-fold versus 12-fold coordination). The effect of the warping terms in the interstitial on the self-consistent energy is found by taking the difference of the muffin-tin and warped-muffin-tin columns in Table I. For bcc iron this yields values of 8.0 and 7.2 mRy/atom, while for fcc iron we obtain the much larger value of 13.0 mRy/atom. If we assume a numerical uncertainty of 1 mRy/atom for the relative value of the energies, which is reasonable in view of our findings pertaining to the k-point convergence, we see that the full potential calculation puts fcc iron 6 ± 1 mRy/atom below bcc ferromagnetic iron in the VWN approximation[1] and 4 ± 1 mRy/atom in the vBH approximation. Our warped-muffin-tin calculation then changes this difference to 2 ± 1 mRy/atom (VWN) and 0 ± 1 mRy/atom (vBH), essentially reproducing the results of Ref. 2. This is consistent with our limited experience[8] of comparing total energies calculated by our full potential method and a linear muffin-tin-orbital method in the atomic-sphere approximation, where for the $3d$ transition metals the latter always seems to put the bcc structure slightly lower in energy than the fcc structure as compared to the full potential method. The difference in energy depends on the size of the muffin-tin radius. In our full potential program we cannot evaluate the effect of overlapping muffin-tin spheres, and hence we have no way of determining the effect of this approximation on the total energy. This is an important question, though, in cases where one is discussing structural energy differences on the order of 1 mRy/atom. Therefore this point needs further investigation.

In this Brief Report we show that the muffin-tin approximation has a non-negligible effect on the total-energy difference between different crystal structures of the same material and when the approximation is avoided, the fcc phase of iron is lower in energy than the bcc

phase. The sphericalization assumption is thus shown to have a more drastic effect on the fcc energies than on the bcc energies. Apparently in this sense we conclude that in density-functional theory the iron atoms in the bcc structure are more spherical than in the fcc structure. This conclusion also points to a cause of the failure of the local-density approximation. At a given time, a specific iron atom will be in one of its multiplet states and certainly nonspherical. The neighboring atoms will then experience a more distorted crystal field

and adjust their electronic structure accordingly. We have concluded that the atoms in bcc iron are more spherical. This indicates that for bcc iron more multiplet states are included in our ground-state density. The difference in energy between the lowest multiplet state and the average as found in our calculation is therefore larger in bcc iron. Allowing the atoms to be in their lowest multiplet state will then lower the energy of ferromagnetic bcc iron more than that of fcc iron and will stabilize bcc iron.

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