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Structural properties of ferromagnetic bcc iron: A failure of the local-spin-density approximation

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The electronic structure and total energy of ferromagnetic bcc iron have been determined theoretically as a function of lattice constant with our numerically very precise, full-potential, linearized-augmented-plane-wave method for three different choices of exchange-correlation functions. Results are presented for equilibrium lattice constant, bulk modulus, and magnetic moment. These results indicate that nonlocal corrections to exchange and correlation are required to local-spin-density-functional theory.

In recent years the local-density approximation has been applied very successfully to evaluate structural properties of solids, thin films, and molecules.[1-6] For the magnetic 3d transition metals, however, a systematic study by Moruzzi, Janak, and Williams[1] showed some serious discrepancies with experiment. The computational method used by these authors relies on the standard muffin-tin approximation and, as a consequence, the origin of these discrepancies is obscured. From their work it is not possible to discern between effects related to the local-density approximation and effects related to the inaccuracy in their computational method. Therefore, a more careful study is necessary in order to describe this situation.

The effect of different choices of the exchange and correlation potential on the electronic band structure of iron has already been investigated by Callaway and Wang;[7] they found only very small changes in the relative positions of the eigenvalues of the effective single-particle equations. An analysis of the de Haas–van Alphen data[8] shows that local-density calculations make an error in the relative positions of the d band and the free-electron-like band; e.g., the minority-spin p-like state N_1', which should be at the Fermi level, is found approximately 40 mRy above the Fermi level. Hence, Callaway and Wang's results lead to the conclusion that within local-density theory one does not recover the experimentally determined Fermi surface. This is not an accurate test of local-density theory, however, since in principle the basic Kohn-Sham equations themselves are not able to predict the shape of the Fermi surface exactly[9] and lead to a presumably small error. On the other hand, structural properties are derived from the total energy which is the fundamental physical quantity of the theory, and, hence, is correctly described by density-functional theory. Further, the total energy is a much more sensitive quantity than the energy spectrum of the effective single-particle equations. Because of this sensitivity, it is imperative to perform numerically accurate electronic structure calculations in order to assess the role of the local-density approximation in the determination of structural properties of the magnetic 3d transition metals. Our newly developed full-potential linearized-augmented-plane-wave (FLAPW) method[2] provides us with a tool that is perfectly suited for these purposes.

The FLAPW method is an all-electron method which makes no shape approximations to the density and the potential for the valence electrons. The present results are obtained by treating the valence electrons in a semirelativistic manner;[10] i.e., the spin-orbit interactions are neglected. Although spin-orbit coupling has noticeable effects on eigenvalues (in the mRy range) whenever degeneracies are removed, these changes occur only in a very small part of the Brillouin zone. In general, the error in the total energy due to the semirelativistic approximation scales with the second power of the fine-structure constant and, hence, will have only a small systematic effect (on the order of 0.1 mRy) on the total energy of Fe. The electrons in the (argon) core are spatially localized to such an extent that they can be accurately dealt with by solving the full Dirac equation for the spherical part of the potential only. The number of basis functions used in the calculations varies between 100 and 150, depending on the location of the wave vector $\vec{k}$ in the irreducible part of the Brillouin zone (IBZ). We have performed self-consistent calculations using 30 as well as 90 $\vec{k}$ points inside the IBZ in order to investigate the accuracy of our results with respect to the numerical integrations in reciprocal space. The remaining absolute error in our total energy is of order 1 mRy, but the relative error (comparing the different calculations) is only 0.1 mRy.

In order to assess the dependence of the results on the choice of exchange and correlation energy function, we have performed the calculations using three different approximations to the local exchange and correlation energy. The exchange energy was approximated by the standard Kohn-Sham-Gaspar form[11] $\alpha\rho^{4/3}$ (KSG) and the correlation energy was either omitted or approximated with either the von Barth and Hedin[12] (vBH) or the Vosko, Wilk, and Nussair[13] (VWN) expressions. The resulting values of the total energy calculated as a function of the volume of the unit cell for these three cases are shown in Fig. 1 together with the experimental value of the equilibrium volume. The solid

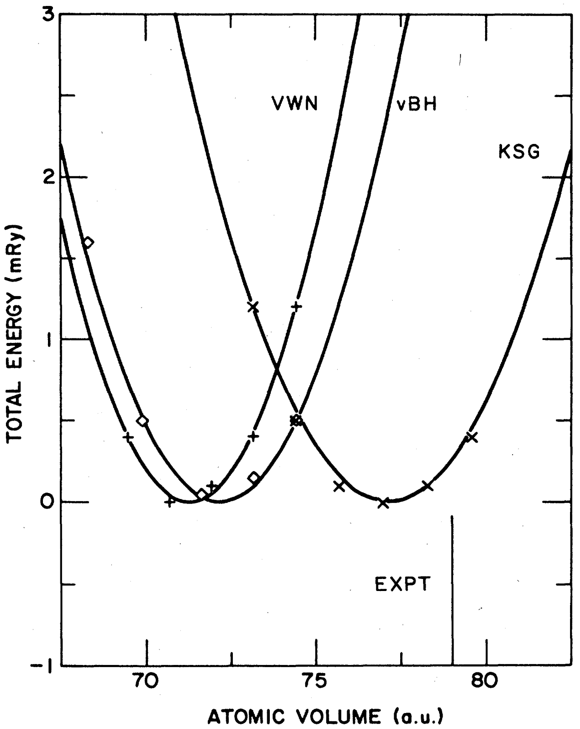

FIG. 1. Total energy (with respect to its minimal value) in mRy as a function of the volume of the unit cell in atomic units for three different approximations to the exchange and correlation energy: KSG stands for Kohn, Sham, and Gaspar; vBH stands for von Barth and Hedin, and VWN stands for Vosko, Wilk, and Nussair. The experimental value of the equilibrium volume is also indicated.

curves are obtained by fitting a parabola to the calculated data points. The energy scales of the three curves in the plot are aligned to give the same energy values at the minima. Although anharmonic terms in the relation between total energy and volume are important in the range of lattice constants under consideration,[2] we do not have sufficient data points to extract accurate values for such terms. One can estimate the effect of these terms on the derived values for the lattice constant and the bulk modulus, however, and we have included this factor in our error analysis. Resulting values for the lattice constant, bulk modulus, magnetic moment, and equilibrium total energy are given in Table I.

Since our FLAPW results based on the vBH approximation to the correlation energy are very similar to those of Moruzzi *et al.*,[1] they indicate that the use of the muffin-tin approximation is reasonable in closed-packed, highly symmetric crystal structures. In these cases, the effects of the nonspherical terms are only weakly volume dependent. On the other hand, one cannot neglect these terms in a comparison of the total energy of different crystal structures.[2] Further, our results show that for ferromagnetic iron the main cause of differences between experiment and theory is related to the use of the local-density approximation.

The calculations employing the KGS potential give the best results for the lattice constant and the bulk modulus but they seriously overestimate the value of the magnetic moment. As usual, the inclusion of additional correlation reduces the magnetic moment,[14] and in this case leads to a value in agreement with experiment. The equilibrium lattice constant as determined by a paramagnetic calculation in the vBH approximation is only 5.13 a.u.[15] This shows that, not surprisingly, magnetism is important in order to obtain agreement with the experimental value of the equilibrium volume. Our results confirm the standard picture that exchange is the most important many-body effect determining the magnetic properties. The effect of correlation on the magnetic moment is relatively small (10%) which is in agreement with the findings of Callaway and Wang.[7] Many-body processes represented in the correlation energy, however, do have a large effect on the structural properties. The change in lattice constant and bulk modulus due to the inclusion of correlation (i.e., use of vBH) is of the same order as the differences between the experimental and theoretical results. Since the error in the correlation energy in the local-density approximation is known[16] to be of the order of 100%, it is likely that calculations employing a more sophisticated approximation to the exchange and correlation energy will be able to reproduce the experimental values. Within the class of local-spin-density approximations to the exchange and correlation energy, the VWN parametrization is presumably the most accurate. These results reproduce the energy of a spin-polarized homogeneous electron gas with an estimated maximum error of 1 mRy.[13] Basically, this parametrization consists of an accurate interpolation between the well-known limits for low and high densities and incorporates Monte Carlo data at intermediate densities. In our case the VWN approximation, however, gives results with the largest errors; this implies that further corrections to the exchange and correlation energy essentially have to be nonlocal. In local-spin-density theory the exchange and correlation energy density at a given point in space is determined only by the electron density at the same point. As a result, pair correlation functions are not well represented[17] and especially the shape of the spin distribution will have an appreciable relative error. This affects the spatial localiza-

TABLE I. Equilibrium values of the lattice constant and bulk modulus in atomic units, the magnetic moment in Bohr magnetons, and the total energy in Ry. The last column lists the uncertainties in our results due to numerical truncations.

	Expt.	KSG	vBH	VWN	Numerical (truncation) error
a	5.4057	5.35	5.24	5.21	0.5%
B	1.14×10^{-2}	1.29×10^{-2}	1.56×10^{-2}	1.85×10^{-2}	10%
μ	2.12	2.29	2.07	2.18	2%
E	· · ·	−2536.725	−2541.100	−2541.195	See text

tion of the *d* electrons and, hence, will have an influence of structural properties like equilibrium values of the lattice constant and bulk modulus.

We have discussed our results for the structural properties of bcc Fe, as obtained with our numerically very precise full-potential, linearized-augmented-plane-wave method. We investigated the effects of three different local approximations to the exchange and correlation energy. Our results show that results obtained with local exchange and correlation potentials are in error. We conclude that necessary corrections have to be of a nonlocal nature, which is not surprising since the local-density approximation does not take into account a correct description of pair correlation functions.

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