Ab initio full-potential study of the structural and magnetic phase stability of iron

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We have investigated the magnetic and structural phase diagram of iron employing the full potential linear augmented plane-wave method within the generalized gradient approximation. Therefore, total-energy calculations have been performed together with investigations with varying c/a ratio to check the phase stability. This study focuses on the structural and magnetic properties relevant to Invar and anti-Invar and structural phase transitions occurring in these materials. We show that the properties of antiferromagnetic fcc iron can be understood by collinear full potential calculations. In order to do this, the antiferromagnetic structure has been distorted by short-range ferromagnetic nearest-neighbor coupling. From this we can conclude that the classical low-spin behavior can be replaced by antiferromagnetic ordering. Additionally, the thermal properties of iron, especially the free-energy and thermal-expansion coefficient $\alpha(T)$ have been analyzed, which is important for the understanding of the anti-Invar effect. The free energy and $\alpha(T)$ were estimated from a Debye scheme for which *ab initio* results were given as input. Besides the more common cubic phases we have investigated hcp Fe at large volumes in view of its magnetic structure. [S0163-1829(99)07929-1]

I. INTRODUCTION

This paper focuses on the magnetovolume instabilities of fcc (γ -)iron, which is an anti-Invar element and also the dominating magnetic element in many Invar and anti-Invar alloys.^{1,2} Iron also undergoes several structural phase transformations driven by pressure or temperature.³

The question of how to explain magnetovolume instabilities, especially Invar and anti-Invar behavior, is discussed from several different standpoints. The first is the traditional high-spin (HS)-low-spin (LS) model that describes anti-Invar as a thermal excitation of the HS high-volume state. The second is the combination of parallel or antiparallel spins with volume fluctuations by using a Ginzburg-Landau formalism.^{4,5} In such investigations the Invar effect is discussed as an anharmonicity in the magnetovolume coupling,⁴ which explains the properties of many Invar alloys.⁶ Nowadays, there is almost no doubt that the anharmonicity is caused by the coexistence of different magnetically ordered states lying close together in energy. Additionally, there exist few other methods that introduce continuous spins in full potential methods to deal with Invar properties. Some pioneering work has been done by Nordström and Singh.

In contrast to local-density approximation (LDA) calculations to describe the ground-state properties of γ -iron, which lead to a perfect degeneration of the nonmagnetic (NM) and antiferromagnetic (AFM) fcc phase, full potential linearaugmented plane-wave (FLAPW) results within the generalized gradient approximation (GGA) show a clear difference in the total energy of the NM and AFM solution.

In this paper we study only collinear spin configurations. The crossing or degeneration of these states may be considered as a hint for noncollinearities. However, we will show that this is sufficient for an at least qualitative, and in many cases even a quantitative understanding of the magnetovolume instabilities and specific features in the physical properties of γ -iron. The spin structure of the fcc phase can be understood from calculations on the basis of a full potential

method combined with the GGA. We have chosen two different AFM structures as representatives from the complex magnetic phase space. The first one is the usual AFM-I with alternating layers of up and down spins, which have the minimal possible frustration [Fig. 1(a)]. The second is an AFM structure, which consists of double layers with ferromagnetic (FM) intralayer coupling, and which we designate as the AFMD (antiferromagnetic double-layer) structure [Fig. 1(b)]. This configuration can be considered as an example of a state with short-range FM order. It has double the number of parallel aligned spins as nearest neighbors as compared to the case in the AFM-I structure. The FM coupling, which is included in the AFMD structure, is important for the discussion of the anti-Invar effect in Fe. In addition to this, the FM and NM states have been calculated.



FIG. 1. Schematic picture of the unit cells used for AFM structures. We used bct cells. The spin direction of the atoms is marked by arrows. The common AFM-I structure is given on the left panel. The c/a ratio is 1 for the bcc and $\sqrt{2}$ for the fcc structure. The AFMD structure is given on the right panel. It consists of two bct cells with $c'/a' = 2\sqrt{2}$ that describes the fcc structure. In the case of bcc (α -) iron, only the AFM-I structure was taken into account.

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All ab initio calculations presented in this work were performed at T=0, because of the lack of an extension of density-functional theory to finite temperatures. This would have allowed a proper treatment of the magnetic structure at T > 0. Therefore, in addition to the first-principles calculations we have made use of a simple Debye-Grüneisen model to account for finite temperature properties. A similar scheme was used by Moruzzi et al. for describing the thermal properties of nonmagnetic materials in the lowtemperature region.⁸ In the second part we focus on hcp (ϵ) -Fe, which occurs in a number of interstitial compounds, which are composed of 25-35 at. % carbon or nitrogen. One interesting question regarding these compounds is the magnetic order of the carbides and nitrides. We derive the magnetic properties of carbides and nitrides of ϵ iron from ab initio calculations in the large volume limit.

 ϵ -Fe can be stabilized under pressure. From experiment it is known that iron undergoes a transformation from the bcc (α) phase into a hcp structure. The critical pressure is about 14 GPa for the $\alpha \rightarrow \epsilon$ transition and about 7 GPa for the reverse transition. We have checked the transition pressure and the equilibrium volume, as well as the magnetization of hcp Fe.

The influence of very high pressures on the structural and elastic behavior of iron was discussed by Söderlind *et al.*⁴⁹ in view of its importance for the earth core. Recently, the $\alpha \rightarrow \epsilon$ transition was studied within a full potential calculation by Ekman *et al.*¹⁰ The authors examined in detail the transformation path from the α ground state to the ϵ phase. In the present paper the volume dependence of the magnetic properties of ϵ -Fe are discussed in detail in addition to the previous works.

II. METHOD

All electronic structure calculations have been performed by using GGA in the Perdew-Wang formula¹¹ for the exchange and correlation energies, which is a suitable tool for 3d elements.^{12,13} This is necessary, because the LDA description is not valid for iron and iron-rich transition-metal alloys. It always leads to a fcc or even a hcp ground state for iron.¹⁴ We used the FLAPW method¹² employing the WIEN95 code developed by Blaha *et al.*,¹⁵ because calculations only taking radially symmetric terms into account would produce a FM ground state for γ -iron.^{16,17} The present calculations have been performed using local orbitals for the 3p states of iron. This extension allows us to use the same energy window for semicore and valence states and prevents the existence of *p*-like ghost bands.¹⁸

The radius of the muffin-tin sphere $R_{\rm MT}$ was chosen to be 2.2 a.u. for all calculated structures. Inside the muffin-tin spheres the potential and charge density are expanded up to an angular momentum of L=6 and higher terms are neglected. For the interstitial region we have used a plane-wave cutoff of $R_{\rm MT} \times K_{\rm max} = 9.0$, which was proved to be accurate for *d* orbitals. The parameter $G_{\rm max}$ controlling the Fourier expansion in the interstitial region was always set to 10.5 Ry^{1/2}. The size of the *k* mesh depends on the crystal structure. We have used a 20×20×20 mesh for the α structure, whereas the close-packed structures have been calculated using slightly smaller meshes. The numbers of *k* points



FIG. 2. Total energies E_{tot} (lower panel) and magnetic moments M (upper panel) of iron obtained from FLAPW calculations within the GGA. Results are shown for the fcc and bcc structures and different magnetic ordering. The solid curves correspond to the fcc phase and the dotted to the bcc phase, respectively. Diamonds indicate NM; squares, FM; and open circles, AFM-I order. Filled circles mark the AFMD state of γ -Fe.

in the irreducible part of the Brillouin zone are 145 for the fcc and 150 for the hcp lattice, and for the AFM-I and the AFMD phase we used 315 and 255 *k* points, respectively. For the calculations involving systems with tetragonal distortions we used 168 *k* points in the irreducible part of the unit cell. The equilibrium volumes V_0 and the bulk moduli B_0 were obtained from fits to Murnaghan's equation of state.¹⁹ In addition to this we give an estimate for the zero-point lattice energy E_D , which is neglected in first-principles methods. A description of this ansatz can be found in the Appendix.

III. RESULTS AND DISCUSSION

A. Cubic iron

The main results of our present calculations for cubic iron are shown in Fig. 2. The FLAPW results for the usual fcc and bcc phases have already been discussed elsewhere.^{20,21} In agreement with experiments we find a FM bcc ground

TABLE I. Calculated atomic volume (V), bulk modulus (B), and magnetic moment (M) of iron for different phases in comparison with the experimental data. The quantities \tilde{B} and \tilde{V} give the results with zero-point energy in the Debye approximation.

System	V (a.u.)	\widetilde{V} (a.u.)	B (Mbar)	\widetilde{B} (Mbar)	$M\left(\mu_B\right)$
bcc					
AFM	74.00	75.08	1.76	1.68	1.25
FM	77.22	77.80	1.74	1.72	2.17
FM expt. ^{a,b}	78.94		1.72		2.22
NM	71.45	71.86	2.79	2.76	0.00
fcc					
AFM-I	72.16	72.98	1.93	1.88	1.30
AFMD	74.37	75.37	1.27	1.23	1.80
AFM expt. ^{a,c}	76.24				0.75
FM/HS	81.16	81.86	1.71	1.69	2.57
FM/LS	71.69	72.18	2.11	2.09	1.02
FM expt. ^a	81.78				
NM	69.79	70.17	2.93	2.90	0.00

^aReference 1 (lattice constant extrapolated to T=0 K).

^bReferences 1 and 37 (*B* and *M* at T=0 K).

^cReference 27 (magnetic moment below T_N).

state for Fe, which is expected for a full potential method within the GGA. The atomic volumes, magnetic moments, and bulk moduli, together with the experimental data, are given in Table I.

The AFM and NM solutions of the bcc phase are energetically unfavorable, having 32.0 and 33.9 mRy higher energies than the FM phase, respectively (cf. Fig. 2). This can be understood from the fact that the calculated NM structure has no direct physical meaning and cannot be compared with the paramagnetic phase that is observed in experiments. From paramagnetic neutron-scattering experiments on bcc iron it is known that there is still a substantial magnetic moment in the paramagnetic phase above T_C .²² These states are also mechanically unstable, which is obvious from totalenergy calculations for constant volume and varying c/a ratio. The corresponding results are displayed in Fig. 3. In the NM or AFM case the slope of the curve at c/a = 1.0 (bcc) leads to a shear constant C' < 0, which means that this solution is not a minimum in energy and, therefore, not stable at T=0. From this we can confirm that the bcc ground state of iron is stabilized by ferromagnetism, which can also be seen from Fig. 2 and Table I. If bcc iron were not ferromagnetic, iron would have a hcp ground state. This confirms the results of the thermodynamical analysis for iron, which was done by Acet et al.²³ It should be mentioned that the FM order must not necessarily be of a long-range type, as was recently discussed by Johnson and Shelton.²

We now focus on the close-packed structures of iron. The most favorable fcc phase has AFM spin order. The total energies of both AFM states are not distinguishable within the accuracy of our calculations. From thin-film calculations of Fe on Cu(100) (Ref. 25) it can be concluded that the degeneracy of the energy is a bulk property. The authors obtained a similar double-layer structure to be most stable for an even number of layers, whereas the AFM-I phase is the most unfavorable AFM state. With an increasing number of layers



FIG. 3. The total energy as a function of the c/a ratio for the equilibrium volume of the FM bcc (squares and dotted line), NM (diamonds), and AFM (circles) fcc (solid line) phases.

the energy difference between the AFM-I and the AFMD state shrinks and it can be assumed that the difference nearly vanishes if the number of layers goes to infinity.

It is obvious that the AFMD state has a higher magnetic moment and a larger equilibrium volume, which is closer to the experimental findings (see Table I). However, it is not completely correct to speak of one minimum. Because of the FM coupling there is a slight indication of a second minimum, although not as clear as in the FM phases (Fig. 2). This double-minimum structure was not observed by Antropov *et al.*²⁶ From linear muffin-tin orbital calculations they also obtained the AFMD structure to be a candidate for the fcc ground state. Unfortunately, their result strongly depends on the set of basis functions and the AFMD state becomes unfavorable if their basis set is expanded.

Nevertheless, since the energy difference between these two minima is zero, for further analysis we neglect the double-minimum structure and describe this state by a single equilibrium volume, magnetic moment, and bulk modulus. Furthermore, the strong anharmonicity of this state suggests the existence of a large number of states with similar energy and volume, which is important in view of magneto-volume effects. The volume difference between bcc FM and fcc AFMD is 2.21 a.u. instead of 4.79 a.u. in the case of the type-I AFM structure, which is still larger than the experimentally measured volume change.³ The anti-Invar effect can be understood from this investigation to be an excitation from an AFM state to a FM/HS phase, where the AFM state already contains short-range FM order. The calculated magnetic moments of the AFM phases are much larger than the moment estimated from experiments performed by Abrahams et al.27

The results of the hyperfine fields $H_{\rm hf}$ of α , γ , and ϵ -Fe calculated by the method of Blügel *et al.*²⁸ are shown in Fig. 4. These results represent quite well the trends found in experiment.²⁹ The absolute values differ slightly from the experimental ones, because of the fact that only the spin part of the hyperfine fields is taken into account. Neglecting the orbital parts leads to a reduced hyperfine field. For AFM γ -Fe the total hyperfine field is very small ($|H_{\rm hf}| \leq 12$ kG),



FIG. 4. Hyperfine fields of α and ϵ -Fe and the ratio of magnetic moment versus hyperfine field, are given in (a) and (c). The results for γ -Fe are given in (b) and (d), respectively. If the unit cells contain more than one atom, only one hyperfine field is displayed here, the others are identical except for the sign. Experimental data (open circles) are taken from Ref. 29. The ratio $M/H_{\rm hf}$, see (c) and (d), is approximately constant for the FM phases and for the γ AFMD structure. In the case of AFM-I γ -Fe, a large peak was detected by this ratio that is connected to the crossover of the hyperfine fields $H_{\rm hf}$ [see (b)].

and Fig. 4 shows that it changes sign at $V \cong 78.0$ a.u. This is close to the volume where the HS state of γ -iron starts (Fig. 2). The hyperfine field of AFMD is ten times larger than in that of AFM-I. It combines the features of both FM and AFM-I. Its volume dependence is already comparable to the γ FM phase.

The conversion factor $M/H_{\rm hf}$ plays an important role for the interpretation and understanding of Mössbauer experiments. It is known that the ratio $M(T)/H_{\rm hf}(T)$ is temperature independent for nearly all systems,^{30,31} therefore, this quantity can also be estimated from T=0 calculations. For α -Fe it was determined to be $M/H_{\rm hf} = 0.0071 \mu_{\rm B}/\rm kG$, which is in good agreement with the experimental value of $0.00625\mu_{\rm B}/\rm kG.^{30}$ The same value was obtained for the FM/HS state in γ -Fe as well as for FM ϵ -Fe. However, in the case of an AFM-I the ratio $M/H_{\rm hf}$ varies strongly with volume, as seen in Fig. 4(b), where a dip is observed near V=78 a.u., which is related to the crossover of the hyperfine field. The calculated ratio $M/H_{\rm hf}$ for AFM-I γ -Fe is in contradiction to the results of Keune et al. who determined a conversion factor of $0.026\mu_{\rm B}/{\rm kG}$ for AFM γ -Fe precipitates in copper.²⁹ The difference between experiment and theory can be understood from the fact that the calculated $H_{\rm hf}$ is much smaller than the experimental value of 28 kG and contrarily, the magnetic moment obtained from the calculations is larger than the experimental value. This leads to an uncertainty in the calculated ratio for AFM-I in γ -Fe. A further aspect is related to this uncertainty. In experiment $M/H_{\rm hf}$ is assumed to be independent of volume changes, which is not true for calculations in the AFM-I structure. Additionally, it should be remembered that the AFM structure of γ -Fe in Cu is not a type-I AFM.³² For the AFMD structure the ratio $M/H_{\rm hf}$ is nearly constant corresponding to $0.019\mu_{\rm B}/{\rm kG}$, which is still smaller than the value obtained from Mössbauer measurements. However, the addition of FM coupling leads to an improvement of agreement with the experimental findings.

In the following part the energetics of iron will be discussed in more detail. The ground-state energy of both AFM γ -phases is 7.43 mRy higher in energy than the FM bcc state. This energy difference ΔE can be related to the experimental temperature of the $\alpha \rightarrow \gamma$ transition, $T_0 = 1183$ K.³ The calculated ΔE corresponds to a transition temperature of 1160 K.

The FM γ phase has two local minima with magnetic moments different from zero. The large volume state with a moment of 2.57 μ_B and V=81.15 a.u. is important for the discussion of magnetovolume instabilities in iron. The present T=0 K calculations can be helpful in order to understand the nature of the magnetovolume effect. Additionally, the investigation of the AFMD structure has already shown that several AFM states can exist having similar energy to that of the AFM-I state. The anti-Invar effect can at least be explained as a transformation from an AFM γ phase to a FM high-spin state (having 3.9 mRy higher energy) caused by thermal excitations.

Allowing for a FM coupling in the AFMD structure leads to a volume enhancement that automatically causes a decrease of the volume difference between the AFM and FM structure. Therefore, the volume enhancement from the AFMD to the FM/HS state amounts to only 5%. Experimentally the relative difference in the volumes at 4 K between the AFM and FM phase is about 7%.¹ In the case of simple type-I AFM, this volume difference amounts to 12% being much larger than the observed value.

It should be mentioned that the FM/HS state, which is discussed here, is at T=0 K mechanically not stable. At $c/a = \sqrt{2}$, which corresponds to the fcc structure, the curvature of the energy curve in Fig. 3 is positive, which is related to a negative shear constant C'. Therefore, thermodynamical fluctuations have to be studied in detail in order to check whether ferromagnetic exchange can be sustained by thermal elastic or magnetic effects.³³

B. Results for finite temperatures

As a step towards understanding the properties of iron, we extend the analysis to finite temperatures by making use of the Debye-Grüneisen model. From this model we can derive the free energy as a function of volume V and temperature T. The free energy F(V,T) and the thermal-expansion coefficient $\alpha(T)$ are handled similarly to the analysis given by Moruzzi et al.⁸ Furthermore, we have obtained the zeropoint energy $E_{\rm D}^0$, which was neglected in the electronic structure calculations. In this model the magnetic contributions to the free energy are included through the anharmonicity of total energies and different magnetic structures. We neglect the contributions from magnons, expecting that they have only minor influence. On the assumption that the entropy of the electronic part can be neglected, the free energy of a vibrating system is composed of the total energy from electronic structure calculations and the free energy of the vibrating lattice, so that

$$F(V,T) = E_{tot}(V) + E_D(V,T) - TS_D(V,T), \qquad (1)$$

with

$$E_{\rm D}(V,T) = \frac{9}{8} k_{\rm B} \Theta_{\rm D} + 3k_{\rm B} T D \left(\frac{\Theta_{\rm D}}{T}\right), \qquad (2)$$

where the first term of $E_D(V,T)$ is E_D^0 . The term S_D is the entropy as given by the Debye formula; E_{tot} is the energy taken from electronic structure calculations. The derivation of E_D^0 together with the empirical correction of the Debye temperature Θ_D , is given in the Appendix. The quantity S_D can be expressed as

$$S_{\rm D}(V,T) = 3k_{\rm B} \left[\frac{4}{3} D\left(\frac{\Theta_{\rm D}}{T} \right) - \ln(1 - e^{-\Theta_{\rm D}/T}) \right].$$
(3)

Here $D(\Theta_D/T)$ is the Debye function, where we have used the common definition given in Ref. 34. This was determined numerically. In order to include the volume dependence in the formula of the free energy, we make use of the fact that $\Theta_{\rm D}/\Theta_{\rm D}^0 = (V_0/V)^{\gamma}$ holds, where $\Theta_{\rm D}^0$ and V_0 are the Debye temperature and volume at T=0, respectively. The exponent γ is the Grüneisen constant. This leads to the following expression for the free energy:

$$F(V,T) = E_{\text{tot}}(V) + \frac{9}{8} k_{\text{B}} \Theta_{\text{D}}^{0} \left(\frac{V_{0}}{V}\right)^{\gamma} - k_{\text{B}} T \left[D \left(\frac{\Theta_{\text{D}}^{0}}{T} \left(\frac{V_{0}}{V}\right)^{\gamma} \right) - 3 \ln(1 - e^{\Theta_{\text{D}}^{0}(V_{0}/V)^{\gamma/T}}) \right].$$

$$(4)$$

There exist two different expressions for γ . The first one derived by Slater³⁵ is

$$\gamma = -g - \frac{\partial^2 P / \partial V^2}{\partial P / \partial V} = -g + \frac{1}{2}(1 + B'), \qquad (5)$$

with g = 2/3. In the second expression g is replaced by 1. This is more appropriate in the low-temperature region.³⁶ B' is the pressure derivative of the bulk modulus. The thermal-expansion coefficient being defined as

$$\alpha(T) = [3V_0(T)]^{-1} \frac{dV_0(T)}{dT}$$
(6)

was determined by numerical derivation of the $\partial F(V,T)/\partial V = 0$ curve.

In the following we present results of finite temperature properties for selected magnetic states of iron. We start with the examination of the influence of $E_{\rm D}^0$ on the volume, bulk modulus, etc. obtained from electronic structure investigations. The addition of $E_{\rm D}^0$ leads to a better agreement with experiment for the value of the volume and the bulk modulus by decreasing B and enlarging V. Similar improvements have been obtained for the transition temperature, which has been estimated from the energy difference between the FM α and AFM-I γ phase. This is 1172 K, compared to 1160 K without $E_{\rm D}^0$. In the case of the AFMD structure the addition of the zero-point energy decreases T_0 to 1109 K compared to the corresponding experimental value of 1183 K. This can be understood from the fact that the large anharmonicity of the AFMD state demands a very small bulk modulus. Therefore, the resulting E_D^0 is smaller than for the AFM-I structure (cf. the Appendix). The addition of E_D^0 leads to a clear distinction of the AFM-I and the AFMD phase.

The results for the volume \tilde{V} and bulk modulus \tilde{B} by including the zero-point lattice energy are summarized in Table I, along with the experimental data. We do not display B' and Θ_D^0 for all phases investigated throughout this work. We note that Θ_D^0 for α -Fe amounts to 467 K, which coincides with the experimental value of 470 K.³⁷ The changes in the lattice constant and bulk modulus are smaller than for the NM elements.¹⁷ Also the volume of the bcc ground state is still smaller than the experimental value (see Table I). However, an extension to finite temperatures within the Debye-Grüneisen model can give some information about phase transformations and the anti-Invar effect of iron. The results for the free energy and thermal expansion obtained from Eqs. (4) and (6) are given in Fig. 5.



FIG. 5. The free energy (upper panel) of α - and γ -Fe as obtained from the Debye-Grüneisen model with full potential electronic data as input. All free energies presented here are given in the high-temperature limit using g = 2/3, see text. This is because the differences in the free energies between the high- and low-temperature limit of the free energies low are very small and cannot be seen in this resolution. The lower panel shows the thermal-expansion coefficient for the same systems as in the upper panel. They were obtained by numerical derivation. The $\alpha(T)$ data obtained from the low-temperature free energy are only given up to 600 K. Thermal-expansion coefficients given up to 1650 K were derived from the high-temperature free energy using g = 2/3. Filled triangles mark the experimental data for fcc and crosses the corresponding ones for bcc iron taken from Refs. 1 and 38.

The free-energy curves run nearly parallel. Only one point of intersection was found between the bcc FM and fcc AFMD solution. Thus, only the $\alpha \rightarrow \gamma$ transition can be described within this scheme. The transition from the γ phase back to a paramagnetic bcc phase at higher temperatures is not included. Even though the γ AFM-I and AFMD states are quasidegenerated in energy at T=0, they show a completely different behavior at finite temperatures. The AFMD phase has a very small bulk modulus (see Table I) combined with large B', which is related to the very broad E(V) curve presented in Fig. 2. However, the intersection allows us to estimate the $\alpha \rightarrow \gamma$ transition temperature from the free energy. It amounts to 1309 K, being in quite good agreement with the experimental data. However, one should keep in mind that the γ AFMD phase still contains AFM coupling that is not found in experiment above $T_{\rm N} = 64$ K. From this point of view the comparison of the transition temperatures is restricted.

In Fig. 5(b), we show $\alpha(T)$ deduced from the free energy together with experimental data. The calculated $\alpha(T)$ data for α -Fe coincides well with experiments for low temperatures (g=1) (Ref. 1) as well as for high temperatures (g=2/3).³⁸ The case of γ -Fe is more complex. As discussed in Sec. III A, the description of the low-temperature phase is not straightforward with respect to electronic structure calcu-

lations. We investigated $\alpha(T)$ of the fcc AFM-I and AFMD phase of iron in the low-temperature limit and, in addition, $\alpha(T)$ was calculated for the fcc FM/HS state. These results are also shown in Fig. 5(b). We find reasonable agreement between the fcc FM/HS solution and the experimental data. In the case of low temperatures ($T \le 150$ K), $\alpha(T)$ of the AFMD phase still coincides with the experimental data (see Ref. 1). Above this temperature, $\alpha(T)$ of the fcc AFMD phase grows rapidly. This would overestimate the anti-Invar effect of iron. Even though no low-temperature experimental data of $\alpha(T)$ of pure fcc iron are available, there are estimations from γ -Fe alloys that determine the maximum of $\alpha(T)$ to be of 26×10^{-6} K⁻¹ at 600 K. In contrast to this value, the calculated value for the AFMD structure at 600 K is 30 $\times 10^{-6}$ K⁻¹, which is also related to the AFM coupling of the AFMD state. It should be mentioned that in the AFM-I structure, $\alpha(T)$ is much smaller and, the thermal expansion of fcc iron even at low temperatures, is underestimated.

The Debye-Grüneisen model gives a reasonable description of the thermal expansion of iron when the data from the electronic structure calculations are sufficiently accurate. The anti-Invar behavior of γ -iron can be partially reproduced and, in particular, the low- and high-temperature regions are in agreement with experiment. In order to describe the medium-temperature range, it is necessary to introduce some statistical weight, which controls the occupation of the the FM/HS and AFMD state. In this paper we assume that the occupation of the states varies linearly with *T*,

$$\alpha^{\text{mix}}(T) = \frac{T_0 - T}{T_0} \alpha^{\text{AFMD}}(T) + \frac{T}{T_0} \alpha^{\text{FM/HS}}(T), \qquad (7)$$

which is a very simple weight function. However, the resulting thermal-expansion coefficient $\alpha^{\min}(T)$ is already in quite good agreement with the experimental findings.¹

C. Hexagonal iron

Iron undergoes under pressure a martensitic transformation from the bcc ground state to the ϵ phase. In this section we discuss the structural and magnetic phase diagram of ϵ -Fe, which we relate to hyperfine field data from Mössbauer experiments. In accordance with these experiments³⁹ we found a NM ground state for hcp iron. The equilibrium volume of this state is 69.6 a.u., which is smaller than the experimental value of 75.23 a.u. found by extrapolating the phase boundary to 0 GPa. Figure 6 shows the calculated volume-dependent total-energy curves of ϵ -Fe and, additionally, the total energy of the bcc FM phase. The calculated critical pressure of the martensitic phase transformation from the FM bcc ground state to the NM hcp phase is about 11.45 GPa, being close to the experimental findings for the $\alpha \rightarrow \epsilon$ transition.^{40,41} In Table II we list the bulk moduli and equilibrium volumes, as well as the magnetic moments of ϵ -Fe. All calculations have been performed by using the ideal c/aratio 1.632, which we received as minimum in energy from a c/a variation at constant volume.

In addition to the NM phase, we have calculated the totalenergy curves of various magnetic phases of ϵ -Fe, where only the simplest type of AFM has been taken into account. A schematic drawing is shown in Fig. 7. For the hcp structure there are again two different FM solutions (see Fig. 6).



FIG. 6. Total energies E_{tot} (lower panel) and magnetic moments M (upper panel) of hcp iron obtained from FLAPW calculations within the GGA. The different symbols mark the different magnetic ordering. The solid curves correspond to the hcp phase, and the dotted to the FM bcc phase, which is plotted as a guideline for the reader. Diamonds indicate the NM; squares, FM; and circles, the AFM order.

Besides a HS state with a magnetic moment of $2.55\mu_B$, there is a LS state which can be stabilized at lower volumes. In contrast to γ -iron the LS state of hcp iron has no moment, which means that it is identical with the NM state. In the case of antiferromagnetism we find a magnetic moment of $0.37\mu_B$. In the range between 72.60 and 81.70 a.u. the AFM state is more stable than the FM and NM states. We find almost the same equilibrium volume for the NM, FM/LS, and AFM phases, which differs from the case of cubic iron. This is expected because of the breakdown of the magnetic

TABLE II. Calculated atomic volumes (V), bulk moduli (B), and magnetic moments (M) for hcp iron in comparison with the experimental data. The calculations have been done within the FLAPW/GGA method (marked with F).

Str	ucture	Method	<i>V</i> (a.u.)	B (Mbar)	$M\left(\mu_B\right)$
hcp	AFM	F	70.19	2.02	0.37
	FM/HS	F	81.19	1.74	2.55
	FM/LS	F	69.32	2.98	0.00
	NM	F	69.64	2.91	0.00
	NM	expt. ^a	70.51 (13 GPa)	2.05	0.00
	NM	expt. ^a	75.23 (0 GPa)		0.00



FIG. 7. Schematic picture of the hcp structure. Arrows mark the spin configuration in the case of AFM. The c/a ratio is 1.632, which corresponds to the ideal ratio.

moment near V_0 . In the case of the AFM solution, there is still a small magnetic moment but this does not produce an observable difference in the total energy.

Pure ϵ -iron can only be stabilized under pressure or epitaxially on substrates and is nonmagnetic. In contrast to this hcp iron alloys show different magnetic features. It has been argued that the structural and magnetic features of carbides and nitrides can be understood from investigations of pure ϵ -iron because of the fact that the N and C atoms sit on interstitial sites and that their influence on the magnetic structure is small. We use ϵ -Fe as a model for hexagonal Fe compounds with nitrogen and carbon as well as for ϵ -Fe-Mn alloys. This approximation is sufficient, as long as the iron concentration is large enough. This means that the *impurity* concentration should not be larger than 25%. Therefore, in Table III our results concerning FM and AFM hcp iron are compared with experimental data of Fe-N, Fe-C, and Fe-Mn systems. They are qualitatively in good agreement with experimental findings. The hcp Fe-Mn alloy has an AFM spin order and the nitrogen and carbon steels that have larger equilibrium volumes are FM. The change of the magnetic structure with the volume is well reproduced by the investigations of pure ϵ -Fe. The moments from the *ab initio* calculations are always larger than the measured data. In the case of Fe_{2.4}C there is no information on the size of the magnetic moment, because this alloy is not stable and it transforms to Fe₅C₂ (χ -carbide). The calculated moment of 2.85 μ_B for the Fe2.4C alloy can be regarded as an upper limit for the magnetic moment.

TABLE III. Volumes (V) and magnetic moments (M) of experimentally determined hcp iron alloys in comparison with the calculated moments and magnetic states for the experimental lattice parameters.

		$M\left(\mu_B\right)$		Magnetic state	
Phase	V (a.u.)	Theory	Expt.	Theory	Expt.
ϵ -Fe(13.6 GPa) ^a	70.51	0.00	0.00	NM	NM
ϵ -Fe ₇₈ Mn ₂₂	77.25	1.50	0.25	AFM	AFM
ϵ -Fe ₃ N ^b	94.46	2.77	1.80	FM/HS	FM/HS
ϵ -Fe _{2.4} C ^c	96.49	2.8	35	FM/HS	FM/HS

^aRef. 39.

^bRef. 47.

^cRef. 48.



FIG. 8. Total energies E_{tot} (lower panel) and magnetic moments M (upper panel) of γ -iron for different gradient approximations. Dotted lines give the results for gradient corrections without angular terms. Solid lines mark the results presented in Sec. III A (full GGA) and dash-dotted lines refer to calculations with the 3p states treated as core states. Circles mark the AFM phase, and squares the FM state. The dotted and dash-dotted curves are shifted by ± 6 mRy against the solid lines as a guide to the eyes.

D. What stabilizes the AFM state in γ -iron?

Iron has been examined with nearly every electronic structure calculation method available. Sometimes the range and the quality of a new approach is judged from its ability to reproduce the observed physical parameters. Therefore, it is an interesting question that is really needed to acquire a good description of iron. It has been shown that a full potential method within the GGA gives satisfactory results in reproducing the structural and magnetic phase diagrams of iron (see Sec. III A and Ref. 21). It is well known that the results become worse if one uses non-full potential methods. In this case the FM/HS state becomes lowest in energy.^{42,43} Using LDA without gradient terms gives a hcp ground state for iron at T=0 and the magnetic moment turns out to be zero.⁴⁴

In this paper we use calculations with FLAPW within the GGA to check what is essentially necessary to stabilize the AFM phase of γ -iron against the FM or the NM phase. The results are summarized in Fig. 8.

First the influence of the angle gradient terms is checked. Therefore, we take only the radial components of the gradient terms into account and neglect all angular-dependent terms, as done in the calculations of Dufek *et al.*⁴⁵

At a first glance the total-energy curves without angular gradients seem not to be very different from the full GGA results, because neither the phase sequence nor the equilibrium volume is remarkably changed. But there is some influence of the GGA on the bulk moduli. In the case of AFM the bulk modulus decreases to 1.8 GPa compared to the value of 1.93 GPa obtained from the full GGA. This is related to the fact that the magnetic moment vanishes already at larger volumes. In the case of FM the bulk modulus is larger (B_{1S}) =1.7 GPa, $B_{\rm HS}$ =2.94 GPa) compared to the original GGA results (see Table I). Apart from these details one can conclude that the influence of the angular-dependent gradient terms is not so essential. But on the other hand it is well known that without the GGA the magnetic moments at V_0 become zero and the FM/LS and AFM solutions vanish. From this one can conclude that the gradients of the spherical terms are very important.

Next, the influence of the 3p states has been examined. The 3p states of iron are semicore states that are not completely located in the muffin-tin sphere. The question is, how important is the small dispersion of these states? In order to answer this question, we calculate the total energy of γ -iron again treating the 3p's as core states. These results are also shown in Fig. 8. The magnetic moment is not affected by this approximation. The same holds for the bulk moduli that are the same as for the calculation with local orbitals (for comparison, see Sec. III A). From these calculations we can conclude that the treatment of the 3p states has no influence on the sequence of phases of γ -Fe.

IV. CONCLUSIONS

In the present paper we have investigated iron within the full potential LAPW method using GGA, which allows an accurate estimation of the structural and magnetic phase diagram at T=0 K. Looking for an explanation of the anti-Invar effect in γ -iron, we first introduced more ferromagnetic coupling into the AFM phase. This step was taken because of the fact that the experimentally detected AFM in fcc iron is not collinear and because of the existence of FM coupling above $T_{\rm N}$. The new state is very close to AFM-I, but its equilibrium volume is shifted to larger volumes and the volume difference ΔV between fcc AFMD and FM/HS decreases, which is in accordance with experimental findings. One can imagine that if one is willing to spend much more computing time in order to investigate larger unit cells, one can observe that the ΔV between the AFM and FM states decreases continuously. Additionally, our calculations were extended to finite temperatures by using a Debye-Grüneisen model to calculate the free-energy and the thermal-expansion coefficient. The results obtained for bcc iron are in excellent agreement with experiment. Similarly, the high-temperature region of fcc iron is well described within this model. Furthermore, it is clear from these investigations that the AFM-I structure does not describe sufficiently the properties of fcc iron. The addition of FM order leads to an improvement of the results, especially in view of the point of intersection of the free energy, which allows a determination of the transition temperature from the bcc to the fcc phase. At very low temperatures the thermal expansion of the AFMD phase is in good agreement with the experimental findings. With increasing temperature the agreement between the AFMD phase and the experiment deteriorates. This is related to the fact that no AFM order exist above T_N .

Our results can be understood as the initial and the final state of the anti-Invar effect of fcc iron. In addition the weighted function $\alpha^{\min}(T)$ gives a qualitative description for the temperature dependence of the thermal expansion of γ -Fe. In order to improve these results we have to use a better statistical weight or to investigate states with less AFM coupling. Furthermore we investigated the volume dependence of ϵ -Fe in view of the influence of nitrogen and carbon. We obtained good agreement with experimental findings as long as the concentration of C or N is not too large.

Finally, we have discussed the terms being relevant to a description of the AFM ground state of iron in the full potential calculations. From our calculations we can conclude that it is mainly the radial terms of the gradients which stabilize the antiferromagnetic order in iron. The angular parts of the gradients and the treatment of the 3p states had only a minor influence.

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APPENDIX

Here we give a detailed description of the calculation of the zero-point lattice energy E_D^0 , employing the formalism developed by Moruzzi *et al.*⁸ In contrast to his work, we calculate the zero-point energy E_D^0 for magnetic systems. It is a known fact that ground-state properties as, for example, the bulk modulus or Debye temperature obtained from totalenergy calculations, are systematically larger than the experimental value and that the equilibrium volume is smaller than the experimental one. One reason for this is that the E_D is neglected. In this paper we give an estimate for E_D^0 , which is determined by use of the Debye formula.

Following Ref. 8 this can be estimated from

$$E_{\rm D}^0 = \frac{9}{8} k_{\rm B} \Theta_{\rm D} \,. \tag{A1}$$

Assuming a constant sound velocity v depending on the bulk modulus B and density ρ through

$$V = \sqrt{\frac{B}{\rho}},\tag{A2}$$



FIG. 9. Longitudinal elastic and the shear constant versus bulk modulus for cubic magnetic crystals. The data points were derived by an analysis of experimental data for single-crystal constants (Ref. 46).

the Debye temperature $\Theta_{\rm D}$ is given by

$$\Theta_{\rm D} = (48\pi^5)^{1/6} \frac{\hbar}{k_{\rm B}} \sqrt{\frac{rB}{M}}.$$
 (A3)

It has been shown by Moruzzi *et al.* and others¹⁷ that this expression for Θ_D is not satisfactory, because the assumption that the sound velocity is proportional to \sqrt{B} is not completely correct. The sound velocity is not direction independent, because it is correlated with the elastic shear and longitudinal elastic constants. For an isotropic medium Anderson⁴⁶ wrote the average of v as

$$v = \frac{\sqrt{SL}}{(\frac{2}{3}L^{3/2} + \frac{1}{3}S^{3/2})^{1/3}}\sqrt{\frac{B}{\rho}},$$
 (A4)

where $\sqrt{L/\rho}$ and $\sqrt{S/\rho}$ are the longitudinal and transversal sound velocities, with the longitudinal and shear constant *L* and *S* for an isotropic crystal, respectively. The constants *S* and *L*, and the bulk modulus are taken from Anderson's work.⁴⁶ In analogy to Moruzzi *et al.* we can show that for magnetic cubic materials the longitudinal and shear constants are also proportional to the bulk modulus. We have determined this proportionality factor by analysis of the experimental data. We found a general factor being valid for magnetic cubic systems, which is shown in Fig. 9.

Employing the results for S and L to Eq. (A4), the sound velocity becomes

$$v = 0.7638 \sqrt{\frac{B}{\rho}}.$$
 (A5)

Therefore, the expression for $\Theta_{\rm D}$ has to be multiplied by the scaling factor 0.7638. Using this relation we have investigated the zero-point energy $E_{\rm D}^0$, which was neglected in the *ab initio* calculation.

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