Amorphous iron revisited: An *ab initio* study

M. Liebs and M. Fähnle

Institut für Physik, Max-Planck-Institut für Metallforschung, Heisenbergstraße 1, D-70569 Stuttgart, Federal Republic of Germany

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The magnetic order in structurally disordered Fe is studied by *ab initio* band-structure calculations which are performed in a fully self-consistent manner with respect to both magnitude and orientation of the local magnetic moments. Several degrees of structural disorder as well as the density dependence of the magnetic state are considered. It is shown that the observed phenomena in amorphous iron can be understood in relation to the magnetic states of fcc iron. At low densities ($\leqslant 7.4$ g/cm^3) amorphous iron remains ferromagnetic, at ≈ 7.9 g/cm^3 competing exchange interactions lead to statistical spin configurations, at higher densities (≈ 8.4 g/cm^3) spatially fluctuating antiferromagnetic couplings result in a smearing of the magnetic states of fcc iron at the corresponding density. [S0163-1829(96)02822-6]

The magnetic state of pure amorphous iron has been under discussion for a long time and the answers given are quite controversial. Because the bulk material of pure amorphous iron is not accessible to experiments, one is left with extrapolations from iron-rich amorphous alloys or experiments on thin films. Extrapolations of the magnetic behavior of amorphous Fe-rich Fe$_{1-c}$Zr$_c$ alloys to pure amorphous Fe lead to the prediction of a spin-glass behavior[1,2] with statistical spin orientations or an asperomagnetic behavior,[3] whereas in thin films of amorphous iron in Y/Fe/Y layered structures no indications for a spin-glass behavior were found.[4] There was much theoretical work on this topic, using a broad variety of methods, but only very few of these methods considered explicitly noncollinear arrangements of local magnetic moments. But this is essential if the objective is to study the magnetic order (or disorder, respectively). Calculations examining noncollinear spin structures in amorphous iron were performed by Krey *et al.*[5] These calculations were based on the tight-binding Hubbard Hamiltonian using an empirical Slater-Koster parametrization and a fitted value for the Hubbard parameter to generate the spin polarization. Lorenz and Hafner[6] performed calculations based on the same model Hamiltonian. Instead of an empirical parametrization they used spin-averaged transfer integrals from a tight-binding linear muffin-tin orbital (LMTO) calculation[7] for a collinear arrangement of local moments. *Ab initio* calculations dealing explicitly with noncollinear arrangements of local magnetic moments were performed for small supercells containing 16 atoms by the present authors.[8] In this paper we present data for larger supercells containing 32 atoms and, more importantly, we demonstrate how the results for the disordered systems can be related to the magnetic features of fcc iron. Furthermore, a comparison of our results with the above-cited tight-binding calculations will be given.

Amorphous metallic alloys can be conceived as randomly and rather densely packed arrangements of atoms. This implies an average number of 12 nearest neighbors like the number of nearest neighbors in crystalline densely packed structures as fcc, e.g. The most important difference in the nearest-neighbor arrangement between the amorphous and the crystalline phases is the broad distribution of nearest-neighbor distances. In order to get an idea of the magnetic

properties of the amorphous state one should therefore start from the fcc phase and study the dependence of the magnetic properties on the interatomic distance. In a second step, we then studied the magnetic properties for several structural models with increasing degree of structural disorder. By this procedure we were able to track the influence of the structural disorder on the magnetic order. As disordered model structures we used periodically repeated cubic supercells, two consisting of 16 atoms and one of 32 atoms. The atomic positions within the supercell were generated by static relaxation of atoms on random positions using simple cubic and quartic pair potentials given by Brandt and Kronmüller.[9] With the supercell consisting of 32 atoms we are able to represent an amorphous structure up to distances of about 2.5 average nearest-neighbor distances in quite good agreement with a reference structure generated in the same way but for a supercell of 2000 atoms. The smaller supercells, consisting of 16 atoms, exhibit a much smaller degree of structural disorder, the most significant feature being the first nearest-neighbor peaks in the pair-correlation functions which have only half the width of the same peak for the 32-atom supercell and the reference structure. The structure called ''16-atom cell (2)'' has a slightly higher degree of structural disorder than the one called ''16-atom cell (1),'' which can be seen in the slightly less structured pair correlation function for radial distances between 1.4 and 2.0 average nearest neighbor distances.

Our *ab initio* calculations of the magnetic properties are based on the density-functional theory making use of the local-spin-density approximation. We use a LMTO method in an atomic-sphere approximation.[10,7] Noncollinear spin structures are treated according to the method of Kübler and co-workers.[11,12] For each structural model and density we performed 5–10 self-consistent *ab initio* calculations, starting from different spin configurations, respectively. We used the method given in our previous paper[8] to choose starting orientations for the local magnetic moments, and additionally we chose random orientations. It is well known that in fcc iron several magnetic configurations are stable or metastable, their energy differences depending sensitively on the density. Among the stable (metastable) configurations are the ferromagnetic, antiferromagnetic, and several noncollinearly
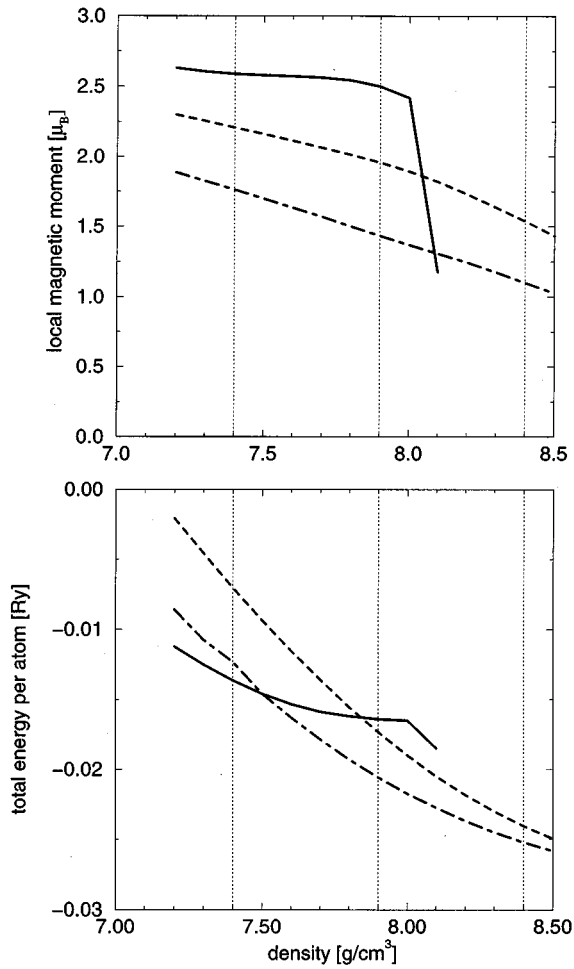
FIG. 1. Properties of fcc iron. Total energy per atom in Ry (lower graph) and magnitude of local magnetic moments (upper graph) in the density range between 7.2 and 8.5 g/cm³ for the ferromagnetic (full line), an antiferromagnetic (dashed line) and one of the noncollinearly ordered (dash-dotted line) states. The noncollinear configuration consists of antiferromagnetically ordered (001) planes with an angle of 90° between the directions of the local magnetic moments in planes succeeding in [001] direction.

ordered states.[13–15] In Fig. 1 we compiled the total energies and the local magnetic moments for the ferromagnetic, an antiferromagnetic and one noncollinearly ordered state for a density range between 7.2 and 8.5 g/cm³, which includes the density one expects for hypothetical amorphous iron (≈ 7.6 g/cm³). The noncollinearly ordered state consists of antiferromagnetically ordered (001) planes with an angle of 90° between the orientations of the local magnetic moments in planes succeeding in [001] direction. According to[16,17] this configuration is one of the energetically lowest noncollinearly ordered states. We investigated the influence of structural disorder on the magnetic order in iron for three densities, namely 7.4 g/cm³ (where in the fcc structure the ferromagnetic order is the most stable one), 7.9 g/cm³ (which is about the density of crystalline bcc iron and where in the fcc structure a noncollinearly ordered state is energetically lowest and the ferromagnetic and antiferromagnetic states are energetically nearly equivalent) and 8.4 g/cm³ (at that density ferromagnetic order with a large magnetic mo-

ment does not exist in the fcc structure). The three densities which we have chosen for our investigation of structurally disordered systems are marked by dotted vertical lines in Fig. 1.

In Table I we compiled the energetically lowest and second-lowest magnetic states which we found, together with a characterization of their orientational configurations and with the magnitudes of local magnetic moments, for the three densities and the three structural models, the structural disorder increasing when going from left to right in the table. For comparison, we give the corresponding information also for the fcc structure. To define what we mean with "statistical" (also called "speromagnetic") and "smeared 90°" configuration we present in Fig. 2 the distributions of the relative angles between neighboring magnetic moments. The "smeared 90°" configuration can be taken as stemming from the noncollinearly ordered state which we considered for fcc iron. We did not perform the calculations for model structure "16-atom cell (1)" at the density of 7.4 g/cm³, but because in the ordered fcc structure and in both structural models with higher degrees of structural disorder the ferromagnetic configuration is the energetically lowest one, there is no reason to expect anything else than ferromagnetic order also for this structural model.

The first fact that becomes obvious from Table I is that the ferromagnetic configuration is stabilized by structural disorder. At 7.4 g/cm³ it is the energetically lowest configuration which we found. At 7.9 g/cm³ it is in the two most disordered structures energetically equivalent to the energetically lowest noncollinear states which we found whereas it is the energetically highest of the three investigated configurations in the fcc structure. At 8.4 g/cm³ structural disorder is even needed for the existence of the ferromagnetically ordered configuration: In the fcc phase and for the structural model with the lowest degree of disorder the ferromagnetic configuration was unstable. In the model structure 16-atom cell (2) it exists but is about 60 meV/atom higher in energy than the lowest configurations we found. The stabilization of the ferromagnetic configuration by structural disorder can be understood as follows. There are two contributions of exchange controlled processes to the total energy, the intraatomic exchange energy, gained by the formation of local magnetic moments, the energy gain being the larger the larger the local magnetic moment is, and the interatomic exchange energy gained by optimizing the orientational configuration. For fcc iron at low density the ferromagnetic state with large magnetic moments and hence with large intraatomic exchange energy gain is preferred. At medium densities there is a compromise between inter- and intra-atomic processes: The interatomic exchange energy is lowered by the formation of an ordered noncollinear configuration (Fig. 2) at the expense of the intraatomic exchange energy (due to the reduction of the magnetic moments). In amorphous iron there are competing exchange interactions at that density which cannot be simultaneously satisfied. As a result, the gain of interatomic exchange energy is limited by disorder and the energy will be optimized by maintaining the ferromagnetic configuration because this configuration yields the largest magnetic moments and hence the largest gain of intraatomic exchange energy.

TABLE I. Results for the magnetic configurations of structurally disordered iron at the three considered densities. The data given are the energetically lowest configuration(s) and the local magnetic moments per atom for these configurations, and in brackets the energetically second-lowest configuration, its local magnetic moments and the energy difference per atom to the lowest configuration.

Density (g/cm^3)	fcc	16-atom cell (1)	16-atom cell (2)	32-atom cell
7.4	Ferrom. $\mu_{loc}=2.6\mu_B$ (Noncoll.) $(\mu_{loc}=2.3\mu_B)$ (18 meV/atom)	Ferrom.	Ferrom. $\mu_{loc}=2.6\pm0.3\mu_B$ (Statistical) $(\mu_{loc}=2.2\pm0.1\mu_B)$ (64 meV/atom)	Ferrom. $\mu_{loc}=2.5\pm0.2\mu_B$ (Statistical) $(\mu_{loc}=2.1\pm0.4\mu_B)$ (20 meV/atom)
7.9	Noncoll. $\mu_{loc}=2.0\mu_B$ (AF) $(\mu_{loc}=1.5\mu_B)$ (44 meV/atom)	Smeared 90° $\mu_{loc}=1.9\pm0.1\mu_B$ (Statistical) $(\mu_{loc}=1.9\pm0.2\mu_B)$ (22 meV/atom)	Smeared 90° and ferrom. $\mu_{loc}=1.9\pm0.1\mu_B$ $2.4\pm0.1\mu_B$, respectively (Statistical) $(\mu_{loc}=1.9\pm0.2\mu_B)$ (13 meV/atom)	Statistical and ferrom. $\mu_{loc}=1.8\pm0.4\mu_B$ $2.2\pm0.3\mu_B$, respectively (Statistical) $(\mu_{loc}=1.8\pm0.5\mu_B)$ (4, . . . ,44 meV/atom)
8.4	Noncoll. $\mu_{loc}=1.6\mu_B$ (AF) $(\mu_{loc}=1.2\mu_B)$ (16 meV/atom)	Smeared 90° and AF $\mu_{loc}=1.5\pm0.1\mu_B$ $1.4\pm0.1\mu_B$, respectively	Smeared 90° and smeared AF $\mu_{loc}=1.6\pm0.2\mu_B$ $1.5\pm0.2\mu_B$, respectively (ferrom.) $(\mu_{loc}=2.1\pm0.1\mu_B)$, (62 meV/atom)	

Statistical configurations (stable or metastable) could be found only for the densities of 7.4 and 7.9 g/cm^3. At 8.4 g/cm^3, self-consistent calculations started with the same angular distribution of the local magnetic moments that lead to statistical configurations at the lower densities evolved either to smeared antiferromagnetic or smeared 90° configurations or even did not converge to a self-consistent state. This means that statistical configurations in the disordered phase are only possible in that range of density where in the fcc phase (Fig. 1) the ferromagnetic and an antiferromagnetic configuration exist. Statistical configurations in the disordered phase are energetically favorable at that density where
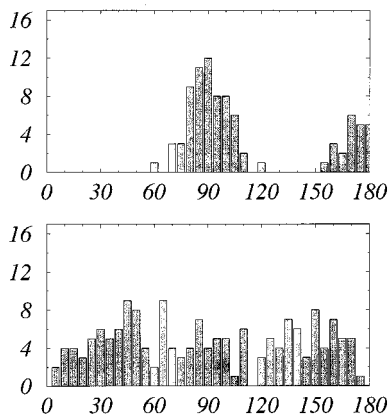

FIG. 2. Terminology for magnetic configurations: Distributions of relative angles (deg) between neighboring magnetic moments in structurally disordered iron. Upper graph, smeared 90° configuration; lower graph, statistical configuration.

in the fcc phase (Fig. 1) the energetical difference between the ferromagnetic and the antiferromagnetic state is very small (and a noncollinear state is energetically lower than these collinear states). If one had made a very crude model for the fcc structure, assigning the density dependence of the energy difference between the ferro- and antiferromagnetic order to the nearest-neighbor exchange integral in a Heisenberg model, the exchange integral would change its sign at that density at which both configurations are energetically equivalent. For a structurally disordered system with just that density one would expect statistically oriented magnetic moments, because there would be a statistical distribution of exchange integrals preferring parallel alignment of neighboring magnetic moments and of those preferring antiparallel alignment. The astonishing fact is that this very crude model (which neglects the existence of noncollinearly ordered states in the fcc structure and the large difference in the magnitude of the local magnetic moments between the different configurations) agrees qualitatively with the results calculated *ab initio*, where all complications neglected in the crude model are included. The interpretation of the statistical configurations at 7.9 g/cm^3 in terms of competing exchange interactions is in agreement with the findings of Sabiryanov et al.,[18] who calculated nearest-neighbor exchange integrals *ab initio* at a density of 7.6 g/cm^3 and found a remarkably large amount of antiferromagnetic interactions. At the higher density, 8.4 g/cm^3, only smeared antiferromagnetic or smeared 90° configurations were energetically low. At that density the ferromagnetic state does not exist in the fcc structure, and in the crude nearest-neighbor Heisenberg model discussed above there are only antiferromagnetic exchange integrals. The ground state of a fcc system with antiferro-

magnetic nearest-neighbor Heisenberg coupling is degenerate[19] because of geometrical frustrations: Perfectly ordered antiferromagnetic planes can be stacked more or less arbitrarily on each other. It is quite obvious that structural disorder introduces spatial fluctuations for the magnitudes of the antiferromagnetic exchange integrals. Thereby, the geometrical frustration of the perfect fcc antiferromagnet is removed and a noncollinear ground state is established where the original spin configurations are smeared out. In reality, fcc iron is more complicated and cannot be described by the crude antiferromagnetic nearest-neighbor Heisenberg model. Nevertheless, the notion that structural disorder results in a smearing of the original spin configurations should be valid. Because for the fcc lattice the energies of the noncollinear spin configuration (with 90° orientation between successive antiferromagnetic layers) and the antiferromagnetic configuration are quite close (Fig. 1) at 8.4 g/cm^3, the structural disorder leads to smeared 90° and smeared antiferromagnetic configurations.

Our results shed some light on the controversial results of the two tight-binding calculations cited above which explicitly deal with noncollinear magnetic structures. The calculations of Krey et al.[5] and those of Lorenz and Hafner[6] use the same form of the model Hamiltonian, but Krey et al. considered a Slater-Koster parametrization of the interatomic matrix elements whereas Lorenz and Hafner used spin-averaged transfer integrals from a tight-binding LMTO calculation for a collinear arrangement of local moments. The result of Krey and co-workers is that for all considered densities (7.39 g/cm^3, 8.21 g/cm^3, and 9.19 g/cm^3) speromagnetic (i.e., statistical) configurations and asperomagnetic configurations (statistical orientation in the upper hemisphere) are energetically equivalent but the average local moments differ by a factor of up to 2 for these two types of configurations. A ferromagnetic configuration with large local magnetic moments was not observed at all. Lorenz and Hafner qualitatively found the same sequence of magnetic states as we obtained for our most disordered structure, i.e., a sequence from ferromagnetic via statistically oriented to smeared antiferromagnetic configurations when increasing the density, with a shift of about 0.5 g/cm^3 to higher densities compared to our data. Smeared 90° configurations were not observed. The crucial question when doing tight-binding band-structure calculations is whether the parameters fitted to a specific set of data are representative for other situations, i.e., whether the parameters are transferable. For the complicated situation of amorphous iron it is not obvious that the same band-structure parameters can be used for all different magnetic configurations, those with large and those with small local magnetic moments, those with antiferromagnetic and those with statistical orientation. Compared to the data of Krey et al., the results of Lorenz and Hafner agree better with our ab initio results, demonstrating that their parametrization is more appropriate for amorphous iron than the parametrization of Slater and Koster.

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