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Electronic structure analysis of the pressure induced metamagnetic transition and magnetovolume anomaly in Fe_3C—cementite

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Abstract

Within the framework of *ab initio* electronic structure calculations we study a mechanism for the recently discovered pressure induced metamagnetic transition in Fe_3C—cementite. It is shown that the transition occurs between a high moment ferromagnetic state and a non-magnetic (non-spin-polarized) state without stabilization of any intermediate antiferromagnetic-like state, which may explain the experimentally observed difference in character of the transitions in Fe_3C and fcc Fe–Pt. Although both materials are Invar-type systems we find considerable differences between their electronic structures and the degrees of *localization*, or *itinerancy*, of the Fe magnetic moments. The possibilities for describing the thermal expansion anomaly in Fe_3C within existing approaches to the Invar problem are discussed in detail.

1. Introduction and preliminary discussion

Fe_3C is the only stable carbide of iron; it crystallizes in the cementite phase with the orthorhombic *Pnma* structure [1]. The interest in this material initially originated from its importance in steel production [2] and in Earth and planetary sciences, where it has been considered one of the candidates for being a major constituent phase for forming the Earth's inner core [3]. During recent years, close experimental attention was paid to the magnetovolume properties of Fe_3C in connection with a significant Invar-type anomaly in its thermal expansion [1, 4, 5] below its magnetic critical temperature ($T_c = 483$ K) [6]. The low, nearly vanishing, thermal expansion below T_c (Invar anomaly) discovered more than 100 years ago in Fe–Ni alloys [7] (and later in a number of other magnetic materials; see [8] for a review) poses a long-standing problem in solid state theory which is still under debate. Among the Invar systems the alloys of Fe are experimentally the most studied and technologically the most important Invar materials, and also have attracted most of the theoretical interest [8]. Fe_3C can be regarded as a highly interesting special case of an Fe based Invar material since

it is a fully ordered stoichiometric compound, while the so-called [8] 'classical' Invar systems like fcc Fe–Ni, Fe–Pt and also bcc Fe–Co are (disordered) alloys. Although some ordered alloy phases, e.g. $Fe_{75}Pt_{25}$, can be prepared, full ordering has never been reached [9], always leaving room for some speculation about the importance of chemical disorder for the Invar phenomena. In addition, the degree of atomic ordering in binary alloys of Fe may change with temperature, which can even result in a chemical order–disorder transition below T_c like in bcc Fe–Co Invar-type alloys [10]. No processes of that kind can be expected for ordered cementite [5]; therefore the recently promoted scenarios of Invar phenomena connected with effects of partial chemical ordering [11] must in this case be ruled out.

Recently Duman *et al* [12], using K-edge x-ray magnetic circular dichroism measurements, observed a sharp pressure induced magnetic transition in Fe_3C under applied pressure of ∼10–12 GPa. They suggested that this transition takes place between a high moment and a low moment magnetic state and linked its occurrence to the Invar properties of cementite within the framework of the discussion given by Entel *et al* [13] for Fe–Ni Invar alloys. The background for such a link is founded on the following arguments: (1) a pressure induced metamagnetic transition has been observed also in Fe–Ni [14] and Fe–Pt [15] Invar alloys; (2) a simple valence electron count [1, 12] suggests, on assuming that carbon contributes its 2p electrons to the Fe d band, that the concentration of Fe valence electrons e/a in Fe_3C is 8.67, which is the about the same number as for the archetypical $Fe_{65}Ni_{35}$ Invar alloy. In [12] it has been noted also that it is an open issue how to explain the difference in character of the pressure induced transitions in $Fe_{72}Pt_{28}$ and Fe_3C, namely the non-hysteretic nature of the transition in Fe_3C as compared to the broad hysteresis found in $Fe_{72}Pt_{28}$ [16]. We wish to point out that some hints concerning the nature of this difference can be found in the experimental observation made by Matsushita *et al* [15] who found that under applied pressure disordered $Fe_{72}Pt_{28}$ alloy forms an intermediate phase (between ferromagnetic (FM) and non-magnetic (NM) phases), which they classified as a spin glass state. Later, first-principles calculations showed [17] that for $Fe_{72}Pt_{28}$ at some volume below the equilibrium, the stabilization of an antiferromagnetic state with respect to both FM and NM states takes place. The stabilization of such intermediate antiferromagnetic-like or spin glass-like states may be a desired 'pinning' entity, which causes the observed hysteresis in $Fe_{72}Pt_{28}$, and if such a feature is absent for Fe_3C it may well serve as an explanation for the difference in character of the transitions between these materials. Later in this paper we will show that a first-principles based analysis similar to those given in [17] indeed does not predict a stabilization of an intermediate spin glass-like phase in Fe_3C.

It also becomes clear that any straightforward generalization of the theories proposed for the anomalous thermal expansion in Fe–Ni and Fe–Pt alloys to the case of Fe_3C must be treated with great care unless a comparison of their actual electronic structures has been made. The simple assumption that carbon provides two electrons to the Fe d band making its structure similar to that in the Fe–Ni case is not obvious and, as will be shown in this paper, is not even true. Apart from the fact that the crystal structures are different, the hybridization of 2p carbon states with 3d Fe introduces entirely new features in the electronic structure which are absent for fcc Fe alloys with transition metals. In addition, one must also note that the experimentally determined atomic moment of Fe (∼1.8 μ_B) in Fe_3C is lower than that in the Invar alloys of Fe–Ni and Fe–Pt, which are strong ferromagnets with a fully occupied majority spin band. The existence of two non-equivalent Fe sublattices in cementite also raises the question [12] of their relative roles in the pressure induced magnetic phase transition and their contribution to the magnetovolume anomaly.

Performing *ab initio* band structure calculations for Fe_3C cementite for various volumes, we will address the above-formulated issues, which mainly originate from the recent high

pressure [12] and thermal expansion [5] experiments. In addition, we will also discuss one particular issue, namely, whether the approach based on the disordered local moment formalism, which has recently been successfully applied to provide an explanation and quantitative estimation of the anomalous spontaneous volume magnetostriction in a couple of fcc Fe based Invar alloys [18–20], can also be applied to cementite.

2. Method and computational details

The electronic structure, total energies and densities of states (DOS) of Fe_3C cementite have been calculated using the *ab initio* Korringa–Kohn–Rostoker (KKR) method in the atomic sphere approximation (ASA) as described in detail in [21, 22]. The effects of exchange and correlation are treated within the framework of the local spin density approximation (LSDA). The ratio of the lattice parameters and internal atomic coordinates of the orthorhombic DO_{11} ($Pnma$) crystal structure of cementite has been fixed to the experimental values determined at $T = 4.2$ K by recent neutron diffraction experiments [5]. Within the range of volumes considered here the possible relative relaxations of the internal coordinates at various volumes are expected to have only a minor effect on the feature of the electronic structure and the calculated total energies as compared to those associated with the volume changes. What is more important for the discussion of the pressure induced magnetic instability and magnetovolume anomaly is a proper choice of the LSDA exchange and correlation potential which will produce an accurate equilibrium volume and equally well treat the non-magnetic (NM) and ferromagnetic (FM) states. The earliest LSDA study of some ground state properties of ferromagnetic cementite at fixed volume was reported by Häglund *et al* [23]. Later Vočadlo *et al* [24] calculated the volume dependence of the total energy of Fe_3C in the LSDA framework employing a full-potential method and the generalized gradient approximation (GGA). They were interested mainly in the equation of state of the non-magnetic cementite at ultrahigh pressures (∼300 GPa), which resembles conditions in the Earth's inner core. At 'lower' pressures their calculations predict a stabilization of the NM state with respect of FM state at the pressures of ∼60 GPa, which is five times more than the experimentally [12] determined pressure where the metamagnetic transition has been observed. The corresponding change in volume which is required [12] to induce the transition is 5%, whereas the GGA estimation [24] is two times larger. Our KKR-ASA calculation with GGA corrections to the LSDA has produced very similar results. In addition, in the case of Fe_3C GGA calculations overestimate the magnetic ground state volume. The problem of the GGA is here related to the well known fact that it tends to overestimate the stability of the magnetic state which cause problems in cases where the NM and FM states are nearly degenerate. A similar problem exists for the strongly exchange enhanced Pauli paramagnet YCo_2 where GGA calculations incorrectly predict a magnetic ground state. It thus appears that the GGA must be rejected as a suitable choice for calculations which are intended to resolve the issues related to the magnetovolume instabilities in Fe_3C, which we have mentioned in the introductory section.

When we apply the LSDA exchange and correlation potential with the exchange part within the local Airy gas (LAG) approximation, as described in [25], we obtain very accurate results (see the next section) concerning the ground state volume and the volume change required to induce the metamagnetic transition. We therefore use this form of the XC potential in our present studies.

All calculations have been converged using a mesh of 1040 k-points in the full Brillouin zone. This k-mesh has been found to be sufficient to ensure a total energy convergence much better than 0.1 mRyd. The size of the ASA spheres has been chosen to be equal for the iron atoms at the 8d and 4c crystallographic positions, whereas the ratio of the radii of iron and

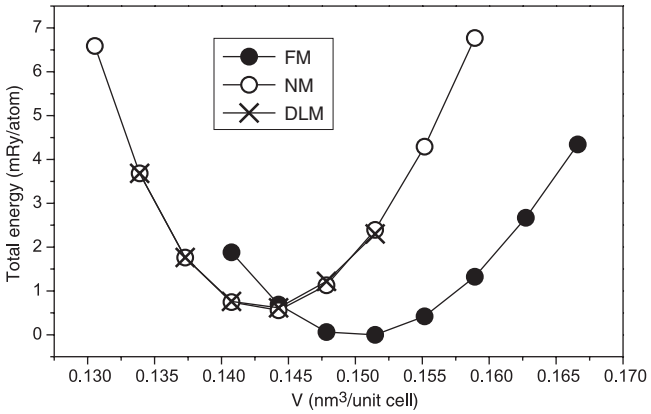

Figure 1. The volume dependences of the total energies of ferromagnetic (FM), non-magnetic (non-spin-polarized, NM) and disordered local moment (DLM) states of Fe_3C.

carbon spheres was set to 0.55. This choice of ASA spheres is demanded by the simultaneous requirements of a minimal overlap and keeping the C sphere at a physically reasonable size. The disordered local moment (DLM) calculations have been performed in the framework developed by Gyorffy *et al* [26]. The use, utility and limitations of the DLM approach for the Invar problem for Fe based transition metal alloys has been discussed in detail in [19, 27].

In this paper the DLM approach is used in two different contexts:

(i) it is used to model the paramagnetic state above the magnetic ordering temperature T_c representing a mean field-like averaging over all possible spin configurations;
(ii) it is applied to describe the actual magnetic ground state ($T = 0$), discriminating between a ferromagnetically ordered state and a state with magnetic moments pointing in random directions (spin glass-like).

In case (i) the DLM approach describes a thermodynamical ensemble average, whereas in case (ii) it provides a 'chemical' averaging over the magnetic configurations at $T = 0$.

3. Results and discussion

The calculated total energy curves of ferromagnetic and non-spin-polarized states are shown in figure 1. The ground state is found to be ferromagnetic with an equilibrium volume of the unit cell $V_0 = 0.150$ nm^3 which agrees well with the experimental value $V_{exp} = 0.151$ nm^3 given by Duman *et al* [12]. The bulk modulus of 203 GPa was calculated from a third-order fit of the FM total energy curve, and is also in reasonable agreement with the experimental [28] value of 174 GPa, being well in the range of the usual LSDA error bar (∼20%) for bulk modulus calculations. The FM curve meets the NM curve at a volume of ∼0.145 nm^3 whereas the volume at which the magnetic transition occurs in the experiment [12, 28] is 0.144 nm^3, so the change in atomic volume required to induce the transition is about 5%.

In the case of the $Fe_{72}Pt_{28}$ Invar alloy, in a similar kind of calculation it has been found [17] that in a certain volume range the disordered local moment state becomes stable with respect to both the NM and FM states, suggesting that at a certain pressure the antiferromagnetic interactions become dominant in these alloys and a spin glass-like state may become stabilized. In contrast to the $Fe_{72}Pt_{28}$ case, the calculated (see figure 1) total energy of the DLM state in Fe_3C is always higher than for FM and NM states. Moreover the self-consistent DLM solution

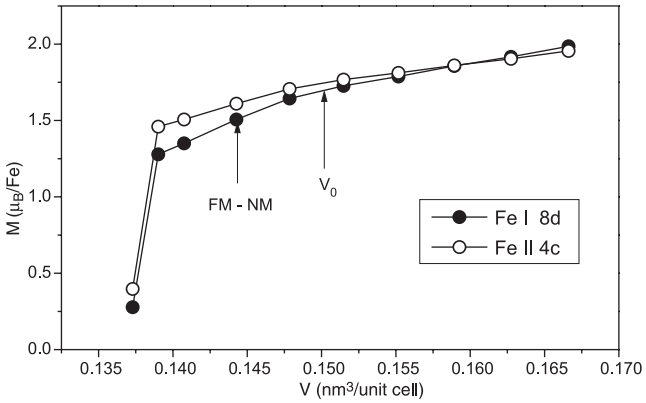

Figure 2. The magnetic moments on the two non-equivalent Fe sites of Fe_3C calculated for different volumes.

with non-zero atomic moments is not stable in this compound at volumes below 0.150 nm^3 (this point will be discussed in more detail below). Some other ordered antiferromagnetic types of structure, e.g. with opposite directions of atomic spins on 8d and 4c positions of Fe, were tried out, but they are also higher in energy than either FM or NM states.

It should be noted, however, that since the crystal structure of cementite is rather complex, it allows for a large number of ways in which antiferromagnetic configurations can be arranged on the lattice and in this respect our search for them is certainly not complete. Nevertheless, our investigation at least does not reveal any tendency for promoting antiferromagnetism at low volumes. The fact that in $Fe_{72}Pt_{28}$ some spin glass-like state is stabilized at high pressures due to a stabilization of AF coupling [17] at lower volume and the absence of this feature for cementite may well explain the weak hysteresis of the transition in cementite as compared to that in $Fe_{72}Pt_{28}$.

In order to discuss the relative roles of the two non-equivalent Fe sublattices in the pressure induced transitions we plot the calculated volume dependence of Fe magnetic moments in the FM state in figure 2. It is interesting to note that at present there exists no experimental information on the site distribution of the magnetic moments even at ambient conditions [5]. It can be seen from figure 2 that the moments on the 8d and 4c Fe sites are only slightly different (at the equilibrium volume: $M_{Fe}(8d) = 1.69\ \mu_B$ and $M_{Fe}(8d) = 1.74\ \mu_B$). The difference increases as the volume decreases, but it remains small at the volume where the pressure induced transition takes place. However, the FM state with high Fe moments exists at lower volumes where it becomes metastable. Only at $V = 0.137$–0.138 nm^3 do the moments in the FM states abruptly become very small ($\sim 0.3\ \mu_B$/Fe). However this low moment FM state is higher in energy than the NM state. Thus it can be concluded that the two Fe sublattices exhibit similar behaviours at the transition, i.e. they lose their moments simultaneously.

Our DLM calculations have indicated an essential difference between Fe_3C and fcc Fe based Invar alloys as well as between pure bcc Fe and Fe_3C concerning the nature of Fe magnetism in these materials. We have found that Fe local moments collapse in the DLM state to very low values and that the energy of such a DLM state calculated for the volumes close to the equilibrium is very close to that for the NM state, being only slightly higher in energy (see figure 1). In contrast to the case for fcc Fe–Ni (Pt, Pd) alloys and also pure bcc Fe, well defined large local moments exist in the DLM state [19]. As is well known (see the extensive discussion in chapters 7, 8 of [29]) this situation suggests a highly itinerant character of the Fe moments in Fe_3C, whereas in bcc Fe and Fe–Pt alloys Fe moments are well localized.

Formally, the comparison of the minimal volumes of the FM and DLM states (figure 1) suggests a large value for the spontaneous volume magnetostriction (∼5%) according to the procedure which worked successfully for strong ferromagnets as described in [18, 19]. However, one cannot consider this result as a satisfactory description of the Invar anomaly in Fe_3C since the DLM description of the paramagnetic state is not adequate in the present case. One must note that the DLM formalism provides a very good description of the paramagnetic state above the magnetic ordering temperature only for systems with well defined local moments, e.g. fcc and bcc Fe based alloys. Its quantitative failure in the case of materials with more itinerant moments, however, does not mean that the origin of the Invar anomaly is different in this case. As has been discussed in detail previously [19], the origin of Invar is a gradual decrease of the locally defined atomic magnetic moments with temperature due to effects of the thermal magnetic disorder. Here the DLM formalism, in the sense of case (i) described at the end of the previous section, is just a static approximation, which describes this phenomenon well for systems with well localized atomic moments. In order to quantitatively describe the case of magnetic systems intermediate between very weak ferromagnets and systems with well defined local moments, one needs to go beyond any static approximation. It thus appears that Fe_3C falls in this class of systems and therefore its thermal expansion anomaly is of very fundamental interest compared to those of 'classical' Fe–Ni Invar.

There is also a fundamental difference in electronic structure between cementite and fcc Fe–Ni alloys, such that the simple link proposed by Duman *et al* [12] (see the introductory section) must be treated with great care. Let us first consider the argument that the concentrations of the d electrons in the two alloys are similar. The direct calculation of the charge transfer between carbon and iron atoms does indeed suggest that some of the carbon 2p electrons become transferred to the Fe sites. In the FM ground state the charge inside the Fe spheres is 8.535 and 8.564 e/atom on 8d and 4c sites, respectively. These values are lower than those (8.67) expected from simple arguments based on the assumption that carbon has provided two electrons to the d band making the d electron concentration similar to that in archetypical $Fe_{65}Ni_{35}$ Invar (8.66). They are much closer to the value 8.5 expected [19] for the fictitious ideal Invar Fe–Pt composition, which is also the electron number at the maximum of the Slater–Pauling curve. However, the analysis of the calculated electronic structure suggests that all such arguments, aiming to established connections between the situations in Fe_3C and Fe–Ni or Fe–Pt alloys, fail. As a matter of fact, the transferred 2p electrons in Fe_3C form a p–d hybrid band which hardly participates in the formation of the Fe moment. In figure 3 we show the calculated total and atom resolved densities of states (DOS) of Fe_3C in the FM ground state. One immediately notices the portion of the DOS between −1.0 and −0.8 Ryd. It corresponds to the Fe–C bonding states. This band is hardly magnetically split and thus does not provide any contribution to the Fe magnetic moment, whereas the d bands of Fe have a spin splitting of the order of 0.2 Ryd. The resulting moments of Fe (∼1.7 μ_B) are even lower than in bcc Fe (2.2 μ_B), whereas in the fcc Invar alloys of Fe with 'similar' valence electron concentrations the moments are much larger (>2.4 μ_B). The Fermi level is located well below the top of the majority spin band of Fe, suggesting also that Fe_3C is a weak ferromagnet in contrast to the strongly ferromagnetic Fe–Pt Invar alloys. In fact, the existence of the p–d hybrid band is the main reason for the relative 'weakening' of the Fe moment in cementite as compared to pure bcc Fe.

4. Conclusions

The results presented in this paper have shown considerable differences in electronic structure and the degree of localization between the magnetic moments in Fe_3C and fcc Fe based alloys. It therefore appears that a straightforward generalization of the theories of Invar anomalies

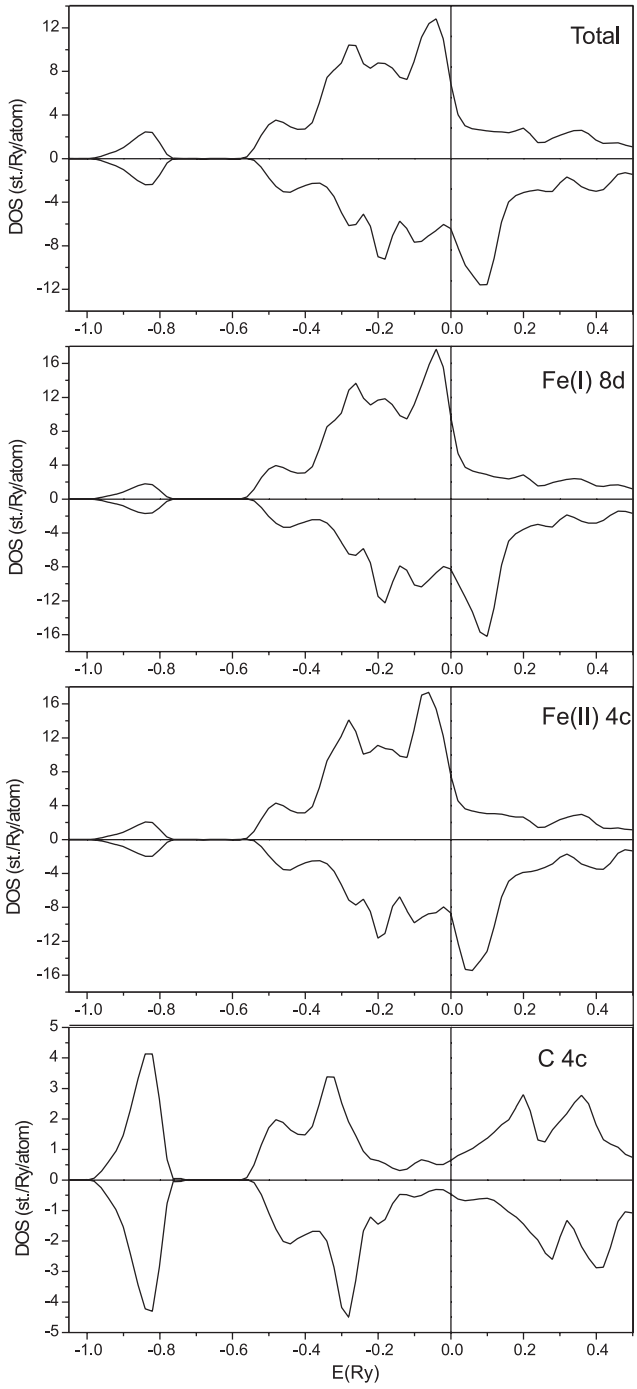

Figure 3. Total and atom resolved densities of states (DOS) of Fe_3C in the FM ground state calculated at the equilibrium volume.

proposed for 'classical' Invar alloys is not applicable. Although the calculations presented provide a very good description of the ground state properties including the pressure induced

magnetic phase transition in cementite, the description of the finite temperature magnetic excitations, which are, in particular, responsible for the Invar anomaly, must go beyond any static approximations like the DLM one in the theory of itinerant magnetism. The reason for this originates from the fact that Fe_3C falls in an intermediate class of systems, between the limits of very weak itinerant ferromagnets and ferromagnets with well defined local moments.

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