First-principles investigation of ferromagnetism and Invar effect in fcc Fe-Cu alloys

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The progress in the preparation of metastable Fe-Cu alloys has recently enabled the experimental determination their magnetic and volume related properties over a wide range of alloy compositions. In this paper we discuss the results of these experiments on the basis of our first-principles calculations. The origin of the Invar effect in these alloys is found to be the same as in Fe-Pt and Fe-Pd and is connected to the weakening of the Fe moment due to effects of thermally induced magnetic disorder. We also explain the behavior of the ferromagnetic ordering temperature with concentration and the Invar effect in fcc Fe-Cu on the basis of an analysis of the electronic structure. We find, in particular, that the effective magnetic interaction between Fe moments shows a pronounced maximum at the composition $Cu_{59}Fe_{41}$, which is related to the peculiarities in the electronic density of states.

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I. INTRODUCTION

The iron alloys with fcc structure attract considerable interest in physics and technology.[1] They show a number of peculiar properties, which have been a subject of gross controversies in solid-state theory. Examples include Invar anomaly,[2] reentrant spin glass behavior, and the like.[3] The key issue in the theory of these alloys is to understand the magnetic properties of Fe in the fcc crystal environment. Up to 1183 K pure Fe crystallizes in the bcc structure where a transition to fcc takes place.[3] A big effort[4] was put into the understanding of a low-temperature magnetic state of pure fcc γ-Fe despite that in nature it is stable only at temperatures much higher than a possible magnetic ordering temperature. Theory based on *ab initio* calculations have predicted an instability of the ferromagnetic ground state at the equilibrium lattice constant in γ-Fe (Ref. 5) and proposed a stabilization of a noncollinear spin-spiral configuration.[4] The experimental verification of these predictions is very difficult since at low temperatures the fcc structure with Fe exists only if it is alloyed with a considerable amount of other metals such as Ni, Pt, or Pd. There where attempts to stabilize pure Fe in the fcc environment by producing Fe films on the top of fcc Cu substrates, however, it has been shown that in these cases even purest ultrathin samples always contain a large amount of bcc Fe precipitates which dominantly define the magnetic behavior.[6] In the case of iron rich Fe-Ni, Fe-Pt, and Fe-Pd alloys it was found that the magnetic moment of Fe is enhanced as compared to its value in pure bcc Fe. Numerous *ab initio* calculations for these alloys are in agreement with this observation. In Fe-Pt(Pd) alloys the lattice constants are much larger than expected for the pure γ-Fe and this is the reason for the stabilization of a high moment state on Fe. In case of Fe-Ni both alloy constituents are magnetic. Supercell calculations suggested that in Fe-Ni there is a continuous manifold of noncollinear spin configurations having lower total energy than the collinear ferromagnetic one,[7] which can also be relevant to the re-entrant spin-glass behavior of ferromagnetic Fe-Ni alloys at very low temperatures.

Recent experiments on Fe-Pt alloys at ultrahigh pressures have suggested by lowering the volume the ferromagnetic state at first becomes unstable with respect to a formation of spin-glass state and only at even lower volume becomes nonmagnetic[8]. The *ab initio* calculations for Fe-Pt are in agreement with this observation predicting the existence of two critical volumes at which the FM state becomes unstable with respect to a state with disordered local moments and a nonmagnetic state, respectively.[9]

All these alloys [fcc Fe-Ni(Pt, Pd)] in the Fe rich region show very small nearly vanishing thermal expansion below the magnetic ordering temperature Invar anomaly[2] and, especially Fe-Ni, is regarded as a so-called "classical" Invar system. Recently we have shown that for Fe-Pt and Fe-Pd alloys good quantitative account for this effect can be provided by *ab intio* calculations employing the disordered local moment (DLM) formalism.[10] The analysis of these results linked[11] the Invar effects in these systems to a gradual weakening of the local Fe moments caused by the changes in the electronic structure due to temperature induced magnetic disorder. This *ab initio* formalism, however, is not directly applicable to the Fe-Ni alloys, since the relatively small Ni moments completely vanish in the DLM state causing an overestimation of the spontaneous magnetostriction by almost a factor 2 (see also the results of the phenomenological theory by Kakehashi[12] for Fe-Ni). Earlier Crisan *et al.*[13] have shown that a DLM description of the Invar effect in Fe-Ni can be adopted on *ab initio* level if one considers the effects of partial chemical ordering which eventually can take place in these alloys. Another famous picture of the Invar anomaly in Fe-Ni alloys was proposed by van Schilfgaarde *et al.*[7] who linked the thermal expansion anomaly to the vanishing nonharmonicity of the lattice vibrations due to the existence of a continuous manifold of noncollinear magnetic configurations with lower total energies and equilibrium volumes than the ferromagnetic one. The problem of the latter approach is that it cannot be adopted for Fe-Pt(Pd) and bcc Fe-Co Invar alloys since there is neither theoretical nor experimental evidence of any stable noncollinear configurations for these alloys. Let us note that despite of the mutual competition of these theories for the cases of Fe-Ni and Fe-Pt one can explicitly rule out the popular two-state Weiss model,[14] often adopted in the literature for phenomenological discussions of

the physical properties of fcc Fe alloys. The two-state model rests on the assumption two separated energy minima at different volumes, which correspond to two different magnetic states. Nowadays (Refs. 7,9) it has become clear that the existence of two separated minima of the total energy which was found in earlier fixed spin moment calculations for Fe-Ni (Ref. 15) and Fe-Pt (Ref. 16) alloys and which supported the speculations about a validity of the Weiss model in the late 1980's and 1990's, is just an artifact of the ferromagnetic constraint being used in these calculations.

II. PROPERTIES OF IRON-COPPER ALLOYS

From the discussion given in the introduction it can be concluded that the problem of Fe magnetism in an fcc environment and its influence on other physical properties such as thermal expansion is still not completely settled, despite the huge progress made during the last decade by the application of the state of the art *ab initio* methods. Further insight into the problem can be provided by studies of magnetism in metastable fcc Fe-Cu alloys. Fcc Cu always has been considered as a promising host for studying the Fe magnetism in an fcc environment: fcc Cu has a lattice constant much smaller than those of Pt and Pd and closer to the value expected for fcc Fe. In addition, in Fe-Cu alloys Cu can be expected to be nonmagnetic which is not the case for Ni in Fe-Ni. Another difference between Fe-Ni and Fe-Cu fcc alloys is that the former due to magnetism of Ni is always a weak ferromagnet whereas fcc Fe-Cu is always in the strongly ferromagnetic regime where the Fe spin up band is fully occupied. The obstacle for the preparation of Fe-Cu alloys is the extremely low miscibility of Fe in Cu being as low as 1–2 % for conventional alloying techniques. However, recently considerable progress in mechanical alloying has allowed to prepare fcc Fe-Cu alloys for the wide range of the alloy compositions and perform measurements of their magnetic properties.[17,18] It has been found[17] that the concentration dependence of the low-temperature saturated magnetization in these alloys follows the well-known Slater-Pauling curve. Only recently the thermal expansion above the room temperature was measured by Gorria *et al.*[18] for three fcc alloy compositions $Fe_{65}Cu_{35}$, $Fe_{44}Cu_{56}$, and $Fe_{16}Cu_{84}$. For the $Fe_{44}Cu_{56}$ sample a pronounced Invar anomaly was observed below the ordering temperature $T_c \approx 350$ K. Let us note an interesting fact related to these finding: it appears that Fe-Cu alloys show the Invar anomaly at the Cu-rich concentrations which is in contrast to the fcc Fe-Ni, Fe-Pt, and Fe-Pd alloys which exhibit an Invar anomaly only on the Fe-rich side.

In this paper we perform first-principles investigations of the electronic structure and magnetism in disordered fcc Fe-Cu alloys employing the disordered local moment formalism and aim to provide an explanation for their observed magnetic properties. We have found that the Invar anomaly in Fe-Cu can be understood and described in a similar way as it was done recently for Fe-Pt, Fe-Pd, and bcc Fe-Co alloys.[11] The calculated spontaneous volume magnetostriction greatly increases as we move to the Fe-rich compositions and may approach values that exceed the maximal values found for Fe-Pt and Fe-Ni alloys by more than 50%. In combination with the low T_c expected in this composition range this may lead to a "giant" thermal expansion anomaly.

We find also that estimated critical temperature of magnetic phase transition exhibits a maximum at the intermediate Cu concentration what can be linked directly to a peculiar concentration dependence of the electronic structure which leads to an increase of the effective magnetic exchange interaction between the Fe moments as the Cu concentration increases. The latter dependence is observed experimentally in stable fcc Fe-Pd and Fe-Ni alloys.[1] However, the measurements[19] reported for Fe-Cu thin films prepared by vapor deposition on various substrates have shown a monotonous increase of T_c with Fe concentration in the whole fcc composition range. This inconsistency of the theoretical predictions and experimental results together with our analysis of the situation, as given in the Sec. V, allows us to draw an important conclusion, namely, that the high temperature behavior of the metastable fcc Fe-Cu alloys in the Fe-rich region seems to be governed by bcc precipitates existing in the nonhomogeneous samples rather than by intrinsic magnetic properties of pure fcc Fe-Cu phases.

We note that electronic structure calculations for some disordered Fe-Cu alloys have been reported earlier[20,21] but they dealt only with the ferromagnetic ground state properties such as magnetic moments and densities of states. Our results concerning the ground state magnetic properties are in good agreement with these calculations[20] and suggest that the $T=0$ K Fe magnetic moment in fcc Fe-Cu alloys is much larger than that estimated from the experimental magnetic measurements on metastable samples.[17] This again may indicate that inhomogeneities, which contain fair amounts of bcc phases (which possess smaller magnetic moments) are always present in metastable fcc Fe-Cu samples. We also note that calculations of small supercells, which ignore effects of chemical disorder in Fe-Cu, for example, as in Ref. 22, may run into trouble especially for those alloys where the Fe concentration is small.[22] At least they are not fully consistent with the CPA results presented here and in Ref. 20 as well with cluster calculations,[21] where the effects of the local environment are taken into the account.

Ab initio calculations are dealing with idealized fully stochiometric crystals whereas experiments are performed on metastable immiscible alloys with poor sample quality. It is therefore too ambitious to hope for good quantitative correspondence between experiment and theory in the present case, especially taking into the account that the experimental results are extremely sensitive to sample preparation, heat treatment, etc. However, nowadays the wide applicability of *ab intio* methods for disordered alloys is well established and their results compare well with experiments performed on good quality samples for a large variety of stable alloys (see, e.g., Ref. 20, and references therein). Since in this respect it cannot be expected that Fe-Cu alloys are a peculiar case, we believe that our results on electronic and magnetic properties of ideal crystalline fcc Fe-Cu can be useful to also understand the peculiar behavior of the metastable nonideal samples. In this sense the situation in metastable Fe-Cu is very similar to metastable Fe-Ag where experimental and theoretical results support each other.[21,23,24]

III. METHOD OF CALCULATION

We base our investigations on the application of the all electron self-consistent tight-binding linear muffin-tin orbital (TB-LMTO) method within the atomic-sphere approximation[25] (ASA) combined with the coherent potential approximation[26] (CPA). The effects of exchange and correlation were treated within the framework of the local-spin-density approximation (LSDA) using the parametrization by Vosko *et al.*[27] Integration in reciprocal space has been carried out using 770**k** points in the irreducible wedge of the fcc Brillouin zone. The idea of the DLM formalism[5] is to represent magnetic disorder within the CPA by treating a binary $Fe_{1-x}Cu_x$ alloy as a pseudoternary alloy $Fe^{+}_{1-x-c}Fe^{-}_{c}Cu_x$, where $1-x-c=n(up)$ is the concentration of Fe atoms with up spin Fe^{+} and $c=n(down)$ of those with down spin Fe^{-}. The case of $c=0$ describes a ferromagnetic solution, while $c=x/2$ represents an antiferromagnetic state (complete DLM) with spin-up and spin-down local moments equipartitionally distributed on the Fe sites. The volumes of the ASA spheres are set to be equal for all atoms. The Cu atoms do not have intrinsic magnetic moments, the small FM moment of 0.04–0.07 μ_B/Cu depending on the alloy composition, is induced by the ordered Fe moments and disappears in the DLM state so that DLM calculations for the three $Fe^{+}_{1-x-c}Fe^{-}_{c}Cu_x$ and the corresponding four component alloy $Fe^{+}_{1-x-c}Fe^{-}_{c}Cu^{+}_{x/2}Cu^{-}_{x/2}$ yield the same result.

The disordered local moment formalism is a well established and widely used[26] method to study the electronic structure changes associated with thermally induced magnetic disorder in magnetic metals and alloys. An extensive discussion of the quantum statistical foundation of this method in combination with LSDA can be found in the original paper by Gyorffy *et al.*[28]

IV. ELECTRONIC STRUCTURE AND THERMAL EXPANSION ANOMALY IN fcc Fe-Cu

In this section we apply the DLM formalism to calculate the concentration dependence of the spontaneous volume magnetostriction in disordered fcc Fe-Cu alloys and discuss the physical origin of the Invar anomaly in these alloys on the basis of the analysis of the calculated density of states (DOS) for both FM and DLM configurations.

The spontaneous volume magnetostriction ω_s, defined as relative difference of the equilibrium volumes of the ferromagnetically ordered and the paramagnetic states, is a fundamental property of any magnetic material and its anomalously high value is the main distinctive feature of all Invar systems.[2] The electronic properties of a true paramagnetic state of a magnetic material with well defined atomic local moments can be approximated by the DLM state[28] corresponding to a mean-field-like directional average over all possible configurations of the atomic moments in the system (complete magnetic disorder). ω_s can be determined from the ab-intio calculations by calculating the relative difference

$$\omega_s = \frac{V(FM) - V(DLM)}{V(DLM)}, \qquad (1)$$

where V(FM) and V(DLM) are the calculated equilibrium volumes for the FM and DLM states correspondingly. The applicability of this procedure for calculating ω_s of course depends on the applicability of the DLM itself, which in turn depends on the degree of the localization of the magnetic moments in the system considered. It has been found[5,26,28] that DLM works well in the case of metallic Fe and Co, but has a problem describing the paramagnetic state for the more itinerant case of fcc Ni where it yields a total collapse of the atomic moments in the paramagnetic state. This is the reason why first-principles DLM calculations of ω_s work well for Fe-Pt (Ref. 11) and Fe-Pd alloys where Pt and Pd are nonmagnetic and as well for bcc Fe-Co,[10] but produce overshooting values for ω_s for Fe-Ni case.[29] Recent DLM calculations have also revealed the excellent agreement between the calculated and experimental values of ω_s in the case of pure hcp Gd (Ref. 30) and the Laves Phase $GdAl_2$,[31] where the Gd 4*f*-magnetic moments are almost perfectly localized. Since in fcc Fe-Cu the only magnetic element is Fe, which is in its high moment magnetic state, the situation concerning the applicability of *ab initio* estimation of ω_s is similar to the case of fcc Fe-Pt(Pd) alloys.

As mentioned in the Introduction the current experimental state of thermal expansion measurements for fcc Fe-Cu alloys allows to claim[18] the existence of a pronounced Invar anomaly in Fe-Cu, but does not allow a direct comparison of the calculated magnetostriction with experiment as in the case of other fcc Fe alloys. The discussion given in the previous paragraph thus intended to make clear why the DLM formalism and consequently the application of Eq. (1) to the case of fcc Fe-Cu is justified and not plagued by the difficulties it meets in Fe-Ni.

In Fig. 1 the calculated ω_s for Fe-Cu alloys are presented. For the matter of comparison the previously calculated[11] ω_s for fcc Fe-Pt alloys are also shown. For the composition $Fe_{44}Cu_{56}$ the estimated $\omega_s \approx 1\%$, which is large enough to cause the significant thermal expansion anomaly detected in experiment[18] below the experimental T_c of about 350 K. The calculated volume magnetostriction increases rapidly as the Fe concentration grows and for compositions close to the martensitic phase boundary, where the fcc and and bcc phases coexist $[x(\mathrm{Fe}) > 0.7]$,[17] it reaches values which even exceed the maximal ω_s observed in Fe-Pt alloys by about 50%. Together with the expected lowering of T_c well below room temperature, this may lead to a pronounced thermal expansion anomaly below T_c. The results presented in Fig. 1 thus suggest that for Fe rich fcc Fe-Cu alloys an extension of thermal expansion measurements to low temperatures may lead to the observation of the strongest Invar anomaly ever found for binary Fe-based alloys.

In Fe-Pt, Fe-Pd and Fe-Co Invar alloys the anomalously high values of ω_S were linked[10,11] to the weakening of the Fe moments due to effects of thermal magnetic disorder on the electronic structure. Exactly the same situation we find in fcc Fe-Cu alloys. The calculated Fe magnetic moments for ferromagnetic and DLM states are shown in Fig. 2. We note that the induced moment on Cu in the ferromagnetic state is less than 0.07 μ_B/Cu and vanishes in the DLM state. In the ferromagnetic ground state the Fe moments are almost concentration independent ($\sim$2.36–2.4 μ_B/Fe) and larger than in pure bcc Fe ($\sim$2.17 μ_B/Fe) resembling the situation found in other fcc Fe based alloys Fe-Pt and Fe-Pd where Fe is in a

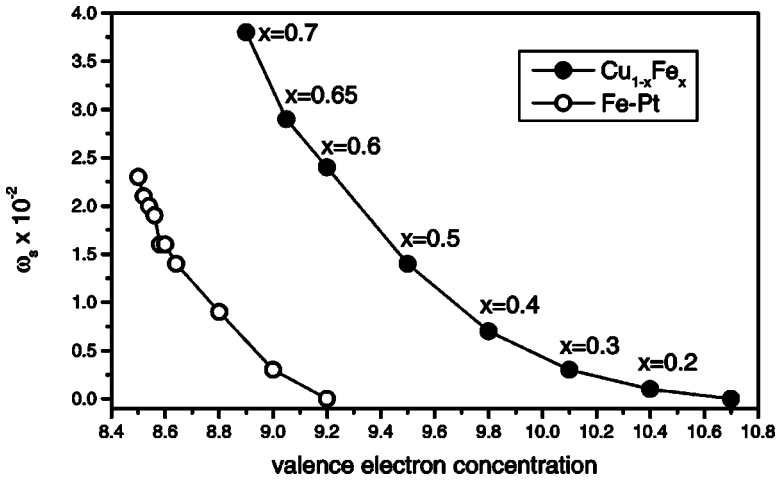

FIG. 1. Calculated concentration dependence of the spontaneous magnetostriction ω_s of fcc Fe-Cu (full circles) and Fe-Pt (open circles).

strongly ferromagnetic state (i.e., Fe 3*d*-majority spinband is completely occupied). The calculated ground-state FM moments of Fe-Cu are also in agreement with earlier calculations by James *et al.*[20] The concentration independence of the FM moment is fully consistent with the experimentally observed[17] Slater-Pauling behavior of the Fe-Cu saturated magnetization at low temperatures.

In the DLM state which represent the paramagnetic state of the alloys above T_c the calculated values of the local Fe moments drops markedly in the Fe rich region with respect of the $T=0$ K ferromagnetic values (Fig. 2). This means that the majority spin-band becomes partially unoccupied in the paramagnetic state. By comparing Fig. 1 and Fig. 2 it is easy to note that the value of ω_s (Fig. 1) directly correlates with the reduction of the moment (Fig. 2). The magnetostriction phenomenon in the itinerant electron systems, i.e., the fact that the equilibrium volume increases (decreases) as the magnetic moments increase, is a direct consequence of the quantum mechanical virial theorem[12] which also rigorously holds in density functional theory.[32]

The large reduction of the local moment in the paramagnetic state in Invar Fe-Cu alloys is thus due to electronic structure effect caused by magnetic disorder and its origin is similar to that in Fe-Pt and Fe-Pd alloys. In Fig. 3 we plot the calculated density of states of three alloy compositions in the FM state (upper panel) and the paramagnetic DLM state (lower panel). In the FM state the Fermi level is well above the top edge of the majority spin band for all alloy compositions presented. In the DLM state the effects of magnetic disorder make the DOS more disperse, similar to chemical disorder, which also makes the DOS of chemically disordered alloys more disperse as compared to the ordered cases. As a result in the paramagnetic state part of the majority spin-band becomes unoccupied and the local on-site Fe moment consequently drops. The effect of the moment reduction is stronger when the Fermi level in the FM state lies closer to the top edge the majority spin-band, which explains why the spontaneous volume magnetostriction increases as the valence electron concentration, or equally the amount of Cu, decreases.

The virtual maximum of ω_s, would be at a concentration where the Fermi level lies exactly at the top of the spin-up band. This is also the condition for the maximum of the Slater-Pauli curve, but these alloy concentrations unfortunately are already outside of the region of Fe-Cu fcc structure stability.

V. EFFECTIVE MAGNETIC INTERACTIONS IN Fe-Cu

In this section we give a discussion of the relative strength of the interaction between Fe moments for different alloy compositions based on the calculated FM and DLM energy

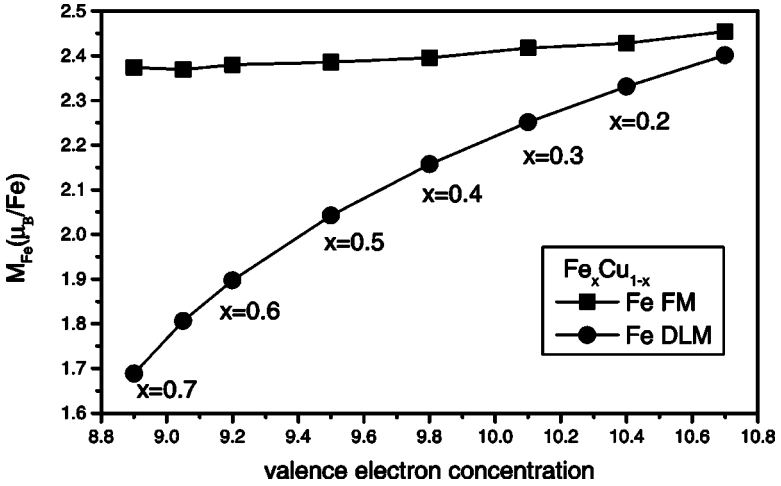

FIG. 2. Calculated magnetic moment on Fe for the FM (squares) and the DLM (circles) state.

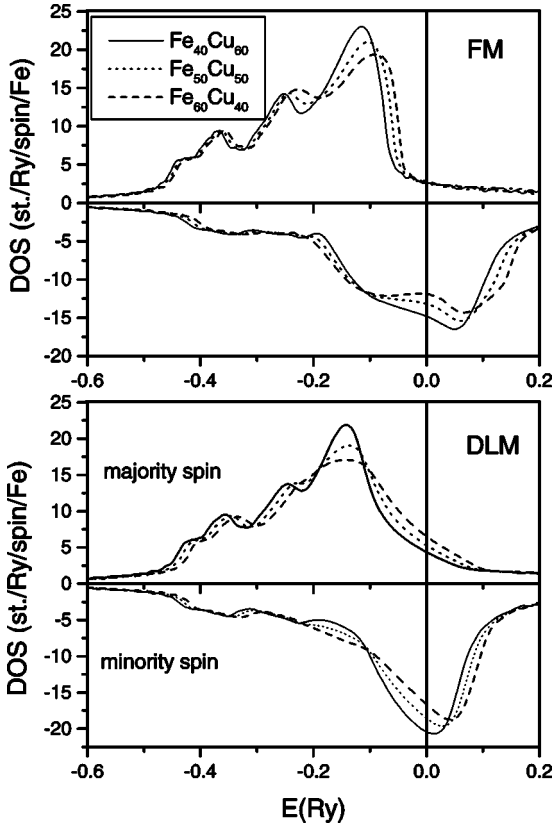

FIG. 3. Density of states for the FM and the DLM state for three different concentrations of disordered Fe-Cu alloys.

differences and densities of states. We assume that the magnetic subsystem of the alloy can be described by a simple classical Heisenberg-type Hamiltonian

$$H = -\sum_{i,j\in\{\mathrm{Fe}\}} J_{ij}\vec{e}_i\vec{e}_j, \tag{2}$$

where $\vec{e}_i$ is a unit vector specifying the direction of the magnetic moment on the ith Fe site and the summation is running only over fcc lattice sites occupied by Fe atoms. The use of the quantum form of the Hamiltonian (2) does not alter the following discussion since we will adopt mean-field considerations only. In the mean-field approach the ferromagnetic critical temperature is proportional to the effective exchange interaction J_0 which is the sum of the all J_{ij} for a single magnetic site

$$k_B T_c = \frac{2}{3}\sum_j J_{0j} = \frac{2}{3}J_0. \tag{3}$$

The total energy calculated for the DLM state corresponds to the average energy over all magnetic configurations with net magnetic moment equal to zero, thus the difference of the FM and DLM total energies, $E(\mathrm{DLM})-E(\mathrm{FM})$, taken for a single magnetic atom in the alloy, directly provides the approximate value of J_0.

In Fig. 4 we plot the dependence of J_0 on the Fe concentration in Fe-Cu alloys calculated in this way. The maximum of the effective interaction at about $Fe_{41}Cu_{59}$ is clearly visible. It suggests also that the composition $Fe_{44}Cu_{56}$ investigated experimentally in Ref. 18 is very close to the optimum, the expected possible further increase in T_c by adding less Fe will not exceed a few percents. Thus the procedure applied above correctly predicts the experimental trend in the changes of T_c with alloy compositions, but it would be far too ambitious to expect that it will also yield the absolute value of T_c. The reasons are the following. (1) It is well known that a mean-field approach for the Hamiltonian [Eq. (2)] overestimates the critical temperature by about 30%. (2) Since we deal with chemically disordered system, we have applied the mean field approximation two times—first for treating magnetic disorder and second for treating chemical disorder. (3) In Sec. III we have seen that the electronic structure and magnetic moments of Fe are not rigid as the magnetic disorder increases, especially in the Invar region, so the J_{ij} in Eq. (2) must have some temperature dependence. If the system is a pure metal with rigid moments (no Invar) such as pure bcc Fe or hcp Gd (no chemical disorder) Eq. (3) has been shown to work rather well and the overestimation for T_c is only 20–30 % as expected.[33] In the present case, for example for the composition $Fe_{56}Cu_{44}$, the calculated critical temperature becomes about 800 K and is thus more then two times larger than the experimental one ($\approx$350 K), which, considering the above mentioned reasons, can still be re-

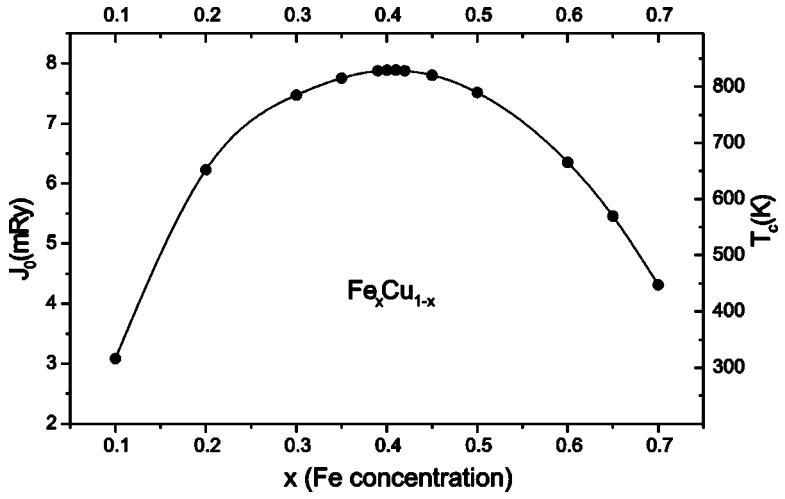

FIG. 4. Concentration dependence of the calculated effective on-site exchange interaction J_0 and the corresponding magnetic ordering temperature T_c as defined in Eq. (3).

garded a as rather fair result. On the right hand side of Fig. 4 we give the scale for the corresponding critical temperature calculated from Eq. (3). In evaluating these values the above-mentioned remarks concerning their mean-field quality should be kept in mind.

The physical origin of the maximum of T_c, or J_0 as shown in Fig. 4 can be understood by recalling the calculated DOS presented in Fig. 3. One obvious mechanism, which leads to a reduction of the effective interaction J_0 as the Fe concentration decreases, is just the reduction of the total number of magnetic atoms in the lattice and therefore the reduction of the terms contributing to the sum in Eq. (3). This implies on the other hand that the existence of the maximum of J_0 must be due to the reduction of the average of the absolute values of the individual two-site interactions J_{ij} as the Fe-Cu alloys become more Fe rich. This reduction can be qualitatively understood using the general RKKY type of relation for the interaction between two magnetic impurities in a metallic host. It suggests that J_{ij} is proportional to $\sin(\eta_l)$ where η_l is the phase shift at the Fermi level defined as in the well known Korringa-Kohn-Rostoker (KKR) method. The phase shift reaches its maximum value when the band resonance of the local magnetic impurity DOS decreases as the Fermi level moves out of it. In Fig. 3 it can be seen that in both FM and DLM states the Fermi levels are shifted out of the peak in the minority spin band as the Fe concentration increases. Whereas it has been very close to this DOS resonance for the extreme case of two isolated Fe impurities in the fcc Cu host. This Fermi level shift happens purely due to the reduction of the electron concentration with Fe substitution into the Cu host and since the majority band is fully occupied. Thus in both cases, in the pure FM state at $T=0$ K and for the DLM state above T_c, the individual pair magnetic interaction between Fe atoms is reduced as the alloy composition becomes more Fe rich. In general the existence of the J_0 maximum is a common property of fcc Fe alloys with nonmagnetic metals that have more valence electrons than Fe. Indeed a similar maximum is observed experimentally in Fe-Pd and Fe-Ni alloys[1] and recently the reduction of the pair interaction strength with Fe alloying was calculated explicitly using the *ab initio* magnetic force theorem for the case of fcc Fe-Au.[34]

However, the experimentally claimed compositional dependence of the magnetic transition temperature of Fe-Cu is not following this trend. It has been found that critical temperature is growing with increasing of Fe concentration up to the fcc-bcc martensite boundary and than jump to even higher values in the region of the bcc phase stability.[19] This is even more surprising if one takes into the account that in the limit of pure fcc Fe it is expected that magnetism must disappears or be, at least, very weak.[1,4,5] Since both the theory presented above and experiments with stable fcc Fe alloys predict the existence of the T_c maximum at some intermediate Fe concentration it can be concluded that at high temperatures the experimentally measured magnetic properties of Fe rich fcc Fe-Cu powder[18] and thin films samples[19] should be related to a large amount of bcc precipitates which have higher T_c. This conclusion is also in agreement with Ref. 5 statements about thin films of Fe-Ni. Since bcc precipitates play a crucial role even for stable Fe-Ni fcc films it may be expected that this is even more true for metastable Fe-Cu films. This could also correlate to the observed non discontinuity[19] in Mössbauer spectra for Fe-Cu films at the martensite phase boundary between fcc and bcc region.

VI. CONCLUSIONS

In conclusion it should be noted that the difficulties in the preparation of the normally immiscible fcc Fe-Cu alloys may normally lead to the samples of much worse quality than for other fcc Fe based Invars such as Fe-Pt and Fe-Pd. Therefore, eventually large amounts of impurities, imperfections and partial phase separation can lead to altered physical properties as compared to the ideal alloys considered in this paper. It is therefore noticeable that we have shown that the Invar effect is an *intrinsic* property of the fully disordered Fe-Cu with Fe concentration more than 30–40 % with ideal fcc structure and its appearance should not be attributed to the nonideality of the samples. The origin of the Invar anomaly is the same as in Fe-Pt and Fe-Pd alloys. We also hope that our prediction of an unusually strong thermal expansion anomaly in the Fe-rich region will stimulate a further experimental activity for these interesting alloys, in particular, concerning lattice expansion at low temperatures, volume properties, and the measurement of ordering temperature dependence on the amount of bcc precipitate phase.

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