Origin of magnetic frustrations in Fe-Ni Invar alloys

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Pair exchange parameters J_{ij} of the classical Heisenberg Hamiltonian for magnetic interactions in the archetypical Invar system, face centered cubic (fcc) Fe-Ni alloys, are calculated from the first principles. The magnetic structure of Fe-Ni alloys in the region of volumes and electron concentrations related to the Invar effect is highly frustrated. However, the origin of such a frustration in concentrated alloys and in the pure fcc Fe are different. While in Fe it is due to the long-range oscillating J_{ij}, in alloys with high Ni concentration it is mainly the consequence of a huge dispersion of the nearest-neighbor exchange parameters, caused by the local environment effects.

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One of the most fascinating phenomena observed in magnetic alloys is the Invar effect. It was discovered at the turn of the 19th century by Guillaume,[1] who found that in face-centered cubic (fcc) Fe-Ni steels the thermal expansion disappeared in a wide temperature range. It has stimulated numerous investigations of iron and iron-based alloys.[2] Recent *ab initio* calculations[3] carried out for a typical Invar system, random fcc Fe-Ni alloys, have shown that at zero temperature the evolution of the magnetic structure is already characterized by a continuous transition from the high-spin ferromagnetic state at large volumes to a disordered noncollinear configuration at smaller volumes. The continuous transition occurs since in the fcc Fe-Ni Invar alloys the magnetic structure is highly frustrated: in a certain volume interval there is a very large number of magnetic configurations, which are energetically very close to each other. This allows the Invar alloy to react on an external perturbation (for example, a change of volume) by the relaxation of its magnetic structure in such a way that the lattice anharmonicity is suppressed.[3,4] The latter is the main reason for the thermal expansion in conventional systems.

The theory presented in Ref. 3 attracted substantial attention in the physical community. For example, in the follow up experimental study, based on the theoretical predictions, the pressure-induced Invar effect was discovered.[5] At this moment, a substantial number of new experiments, which were directly motivated by the theory, are being carried out. For example, pressure dependences of bulk modulus[5] and magnetization[6] in FeNi alloys measured in diamond-anvil cell experiments are remarkably close to the theoretical predictions, while the bulk modulus derived from the ultrasonic experiment seems to behave differently.[7] Neutron scattering experiments with polarization analysis indicate that while the magnetic structure of the Fe-Ni alloy could be close to collinear on an atomic scale at ambient pressure, noncollinear structures may exist over longer length scale.[8] With increasing pressure, an observation of a magnetic phase transition in Fe-Ni alloy was reported by Matsushita *et al.*,[9] while Foy *et al.*[10] observed magnetic instabilities in fcc Fe-Ni thin films that might be associated with noncollinear spin alignments of Fe atoms. At the same time, a theoretical understanding of the origin of the frustrated magnetism in Invar systems is currently absent. In this paper we solve this problem by studying exchange interactions in fcc Fe-Ni alloys.

We have calculated the so-called pair exchange parameters J_{ij} of the classical Heisenberg Hamiltonian $H_{\mathrm{ex}} = -\Sigma'_{ij} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j$ ($\mathbf{e}_i$ is the unit vector in the direction of the magnetic moment of an atom at site i, and the summation runs over all sites i,j, excluding $i=j$) from first-principles density functional theory, using the atomic sphere approximation and the Green's function technique,[11] as well as the magnetic force theorem.[12] The latter has been successfully used in many studies of the exchange parameters in magnetic materials.[13–15] Since we are primarily concerned with the general behavior of exchange interactions, we use the local spin density approximation (LSDA) for the exchange-correlation functional, and the basis set cutoff $l_{\max}=2$. For the same reason we do not correct the exchange parameters by including a renormalization term due to transverse magnetic field constrain, which was recently derived by Bruno.[16] We consider completely random alloys, which is in fact a very good approximation, according to the recent experimental data.[17] The disorder was simulated in two ways, by means of a supercell approach as well as within the coherent potential approximation (CPA). In the latter case the alloy exchange interactions were obtained as described in Ref. 12 by using the CPA site-off-diagonal Green's function.[18]

Let us first discuss some very general features of the behavior of the magnetic interactions in fcc Fe. In Fig. 1(a) we show the pair exchange parameters for the first four coordination shells in fcc Fe as a function of atomic volume. We also show the so-called effective exchange parameter $J_0 = \Sigma_{j\neq 0} J_{0j}$. Note that all the calculations have been done in the ferromagnetic state. The electronic structure and magnetic moments at each atomic volume were fully relaxed. The dependence of the total energy and magnetic moment on the volume is the same as in Ref. 4. The effective exchange parameter J_0, which is shown in the figure by the black solid line, exhibits a well known behavior.[13] It is negative for volumes between 74 and 80 a.u.^{3} and positive (a tendency towards the ferromagnetic order) for larger volumes. Moreover, in the transition region, which corresponds to volumes

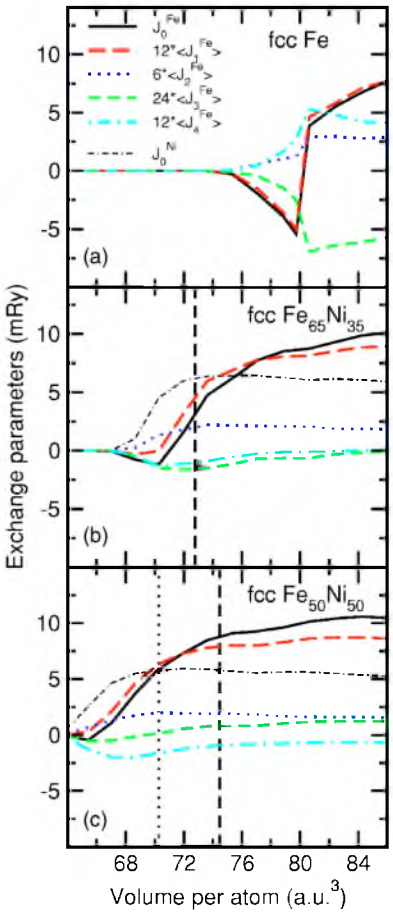

FIG. 1. (Color online) Effective exchange parameters for Fe J_0^{Fe} (thick black solid line) and Ni J_0^{Ni} (thin black dot-double dashed line), as well as average pair exchange parameters $\langle J_p^{\mathrm{Fe}}\rangle = (1/z_p)\Sigma_{j\in p}[cJ_{0j}^{\mathrm{Fe\text{-}Fe}} + (1-c)J_{0j}^{\mathrm{Fe\text{-}Ni}}]$ for the first (red long-dashed line), second (dark blue dotted line), third (green short-dashed line), and fourth (light blue dot-dashed line) shells in (a) fcc Fe, (b) $Fe_{65}Ni_{35}$ alloy, and (c) $Fe_{50}Ni_{50}$ alloy as a function of the volume per atom. z_p is the coordination number of the pth coordination shell, and c is the Fe concentration. In the figure $\langle J_p^{\mathrm{Fe}}\rangle$ are multiplied with z_p in order to show their actual contribution to J_0^{Fe}. Vertical dashed lines in (b) and (c) show calculated equilibrium volume at corresponding concentrations. The vertical dotted line in (c) indicates estimated volume where fcc $Fe_{50}Ni_{50}$ alloy shows Invar behavior under pressure, Ref. 5. Calculations are done within the coherent potential approximation (see text for the discussion).

where noncollinear (in particular spin-spiral) magnetic states become stable,[19–22] our calculations show that although the strongest contribution to J_0 comes from the first five coordination shells, the contribution from other coordination shells is not negligible at least up to the 30th coordination shell.[23]

To analyze the role of the exchange interactions in the energetics of magnetic structures in fcc Fe we Fourier transform J_{ij}, $J(\mathbf{q}) = \Sigma_j J_{0j} \exp(-i\mathbf{q}\cdot\mathbf{R}_{0j})$. $J(\mathbf{q})$ (taken with an opposite sign) has the physical meaning of the energy of the spin spiral with wave vector $\mathbf{q}$. In Fig. 2 $J(\mathbf{q})$ is shown at atomic volume 77 a.u.^{3} This is very close to the equilibrium volume of fcc Cu, which is often used as a matrix for growing fcc Fe precipitates. As one can see in the figure, there are minima of $-J(\mathbf{q})$ close to the X point. The contribution of the

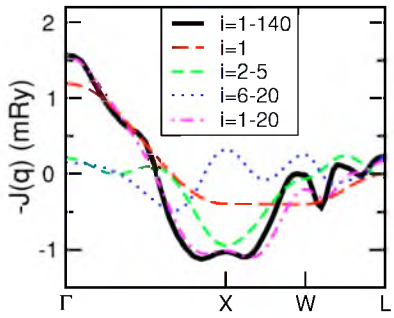

FIG. 2. (Color online) Energy of spin spiral in pure fcc Fe at atomic volume 77 a.u.^{3} as a function of the spin-spiral wave vector $\mathbf{q}$. The energy is estimated as $-J(\mathbf{q})$, and it is obtained from different sets of pair exchange parameters included in the Fourier-transform of J_{ij}, see text.

nearest-neighbor interaction basically makes ferromagnetic state unstable by shifting $-J(\mathbf{q}=0)$ up in energy (for large volumes J_1 has an opposite sign and therefore it stabilizes the ferromagnetic state). If one considers coordination shells 2 to 5, the interactions at these shells collectively stabilize the antiferromagnetic state with $\mathbf{q}$ in the X point of the Brillouin zone. At the same time more distant interactions make this particular antiferromagnetic state unstable and induce frustration by imposing two close energy minima. This is just a qualitative picture, since $J(\mathbf{q})$ is obtained for the (LSDA) magnetic moment (0.82 μ_B) of the ferromagnetic state at this particular volume. In the direct spin-spiral calculations (for the latest see Refs. 21 and 22) where the magnetic moment can relax with the $\mathbf{q}$ vector, those minima are shifted further away from the X point, but more importantly they become very shallow and therefore the ground state is much more frustrated.

Let us now multiply the pair exchange parameters by the corresponding coordination number z_p in order to show their actual contribution to the effective exchange interaction $J_0 = \Sigma_p z_p J_p$, where J_p is the pair exchange parameters at the pth coordination shell [see Fig. 1(a)]. One immediately notices the most spectacular behavior of the interactions in fcc Fe: The effective exchange interaction J_0 is almost entirely determined by the pair exchange parameters at the first coordination shell J_1 (red long-dashed line in the figure). At the same time, the more distant pair exchange parameters are comparable with J_1, nevertheless their contribution to J_0 is almost exactly cancelled due to their oscillating sign.

Note that a system with *infinitely* long-range, oscillating exchange interactions with an average equal to zero corresponds to an exactly treatable model of spin glasses (for a review, see Ref. 24). According to the modern concept of a "broken replica symmetry,"[24,25] spin glasses are considered as systems with infinitely large number of local free energy minima separated by infinitely small barriers. This resembles the situation in pure fcc Fe for all the interactions, except the nearest-neighbor exchange parameter, which shows a clear tendency towards ferromagnetism or antiferromagnetism, depending on the volume. Thus, one can view the situation in the fcc Fe as a *competition* between the tendency towards ferromagnetic or antiferromagnetic order (due to the nearest-neighbor exchange) and a tendency towards the formation of

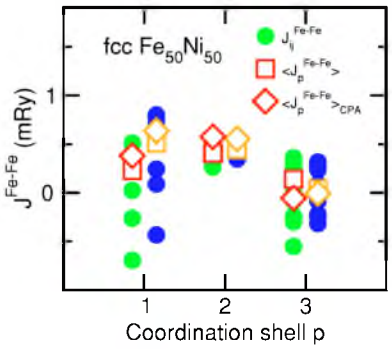

FIG. 3. (Color online) Pair exchange parameters between different Fe-Fe pairs as a function of coordination shell p in fcc $Fe_{50}Ni_{50}$ alloy simulated by 16 atom supercell (Ref. 26) at theoretical equilibrium volume 73.6 a.u.^{3} (filled blue circles, slightly shifted to the right off tick marks) and at compressed volume 70.3 a.u.^{3} (filled green circles, shifted to the left off tick marks). Average values of the pair exchange parameters $\langle J_p^{\text{Fe-Fe}} \rangle$ between all Fe-Fe pairs in the supercell that belong to the pth coordination shell are indicated with open squares. They are in perfect agreement with values obtained by the CPA (open diamonds).

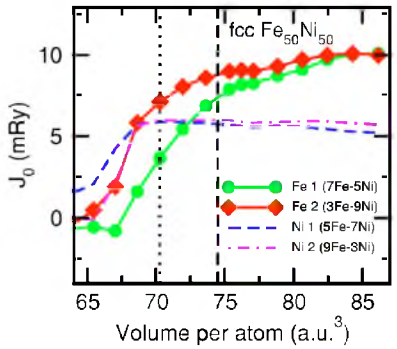

FIG. 4. (Color online) Effective exchange parameters J_0 at two nonequivalent Fe sites and two nonequivalent Ni sites in 16-atom supercell (Ref. 26) as a function of volume per atom. Occupation of the first neighboring shell for each site is given in the legend box. Vertical lines have the same meaning as in Fig. 1.

the spin-glass structure (due to peculiar behavior of more distant exchange parameters). Although this is a highly idealized picture, it is obvious, that it reflects some features of the magnetic interactions in the fcc Fe, and it naturally explains the appearance of many magnetic configurations with almost the same energy in the fcc Fe, which are present exactly in the same volume interval where the peculiarity of the exchange interactions occurs.[20] We therefore may argue that the origin of magnetic frustrations in the fcc Fe is related to the peculiar behavior of its exchange parameters.

Next, let us see if the situation changes in alloys. In Figs. 1(b) and 1(c) we show the effective and pair exchange parameters in the fcc $Fe_{65}Ni_{35}$ and $Fe_{50}Ni_{50}$ calculated within the CPA. Note that the former alloy shows Invar anomaly at ambient pressure, i.e., at equilibrium volume indicated with dashed vertical line in the figure. The latter alloy has the usual thermal expansion at equilibrium volume, but it becomes Invar upon compression,[5] and the estimated theoretical volume where $Fe_{50}Ni_{50}$ should show the Invar behavior is indicated with a vertical dotted line in Fig. 1(c). Analyzing the figures, one can first of all see that the effective exchange parameter of Ni remains practically constant for all volumes at interest. This is in agreement with observation made in Ref. 3, where it was found that Ni moments stay almost collinear and parallel to the direction of net magnetization. Second, we see that the peculiarity observed for the fcc Fe and discussed above weakens with increasing Ni concentration. In the $Fe_{65}Ni_{35}$ the competing character of exchange interactions is still quite pronounced, but it is already quite weak in $Fe_{50}Ni_{50}$. Thus, there must exist an additional reason for magnetic frustrations in alloys.

In Fig. 3 we show the exchange parameters in the random fcc $Fe_{50}Ni_{50}$ alloy between different Fe-Fe pairs at the first three coordination shells calculated for a 16-atom supercell which represents random equiatomic alloy.[26] We choose the small supercell in order to simplify the analysis. It will be clear from the discussion below that the effect observed in our study can only be enhanced in larger supercells. Note also that the mean values of the exchange parameters, indicated by squares in Fig. 3, are in perfect agreement with the values obtained from CPA calculations (shown with diamonds in the figure), indicating the reliability of the above approximation, as well as justifying the use of the 16-atom supercell.

The most remarkable feature seen in Fig. 3 is that the values of the exchange parameters show a huge dispersion for different Fe-Fe pairs at the *same* coordination shell. The tendency increases with decreasing volume. The origin of the dispersion is an extreme sensitivity of the exchange interactions to the local environments of the atoms. For instance, the Fe atoms, which are mostly surrounded by Ni atoms in the first coordination shell have the lowest (negative at both volumes) value of the pair exchange parameter at the first coordination shell, and vice versa, the Fe atoms mostly surrounded by Fe atoms in the first coordination shell have the highest pair exchange parameter. Of course, the pair interactions at the particular shell cannot yield a quantitatively correct picture of magnetic ordering in the system. It is also obvious that the dispersion of the exchange interactions cannot lead on its own to the existence of multiple magnetic solutions, because if all the interactions are positive, the ground state would still be ferromagnetic. To introduce a frustration one needs interactions which have approximately the same value, but are of *opposite* sign (similar to the criteria for the existence of a spin-glass state). As one can see in Fig. 3 this is the case of lower volume where the strongest interactions at the first coordination shell are distributed almost symmetrically with respect to the zero line. At the same time for the higher volume the positive interactions dominate, and therefore they should lead to the ferromagnetic ground state.

To elucidate this point, we show in Fig. 4 the volume dependence of effective exchange parameters J_0 at two nonequivalent Fe sites in the supercell, with different local surroundings. At large volumes the difference is negligible, it increases at equilibrium volume, but both exchange parameters are still large and positive, in agreement with the fact that equiatomic alloy is ferromagnetic at ambient pressure. With further decreasing volume the exchange parameters

rapidly decrease, while the difference between them increases. In particular, they cross zero line at different volumes. For comparison, we also show J_0 at Ni sites. We do not see any anomalous behavior for them in the volume interval of interest.

Because J_0, as calculated in this work, indicates a tendency of the spin at a particular site to rotate from its original direction in the ferromagnetic system, we see that this tendency differs substantially between different atoms in the alloy, being stronger for Fe atoms with more Fe neighbors. In a random alloy, with small short-range order (SRO) parameters such a variation of the local environment is more pronounced than in alloys with either strong ordering effects, or with a tendency towards chemical clustering. This is exactly the case of FeNi alloys[10] where the SRO parameter at the first two coordination shells, reported in Ref. 17 are 3–4 times smaller than they are in CuAu alloys (see, for instance, Ref. 27) at the same temperature 750 K. This means that random chemical environment of real FeNi alloys provides additional source for the frustration of magnetic interactions and they should be much stronger than in our 16-atom supercell.

In summary, we have studied the exchange parameters in fcc Fe-Ni alloys from the first-principles with the aim to identify the origin of the complicated noncollinear structures in the Fe-Ni Invar alloys. In the case of pure fcc Fe the magnetic frustrations are a consequence of the competition between a tendency towards long-range order due to the nearest-neighbor exchange interaction and a tendency towards the formation of a spin-glass-like state due to long-range and oscillating behavior of the more distant exchange interactions, which cancel each others contribution to the effective exchange parameter almost exactly. However, in concentrated random alloys this picture is gradually taken over by the frustration effects related to a huge dispersion of the exchange interactions at the same coordination shell. The strong volume dependence and increasing dispersion of exchange parameters with decreasing volume provides the genesis of the magnetic configuration and makes thereby the magnetic energy volume dependent, which is the necessary condition for the Invar effect.[3]

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