Effective ab initio Exchange Integrals and Magnetic Phase Transition in fcc Fe and Mn Antiferromagnets

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With fcc iron as an example, it is shown that a set of effective exchange integrals, obtained simply by fitting to the total energy of frozen collinear magnon states within the local spin-density approximation, reproduces the energy dispersion of the spiral spin-density wave in remarkable agreement with previous direct theoretical calculations. Monte Carlo simulation is used in the search of the ground spin configuration and in the study of the spin orientational fluctuation behaviors at finite temperature. The Néel temperature thus obtained for antiferromagnetic fcc Fe and Mn is in reasonable agreement with the experimental measurement. [S0163-1829(99)06813-7]

Tremendous success has been achieved in *ab initio* studies of $3d$ itinerant magnetism at zero temperature in the last few decades. For example, for any given collinear and spiral spin-density wave (SSDW) configuration, the calculation of the total energy, usually in the local spin-density functional approximation (LSDA), has been well tested. On the contrary, the thermodynamic behavior, including the magnetic phase transition and the determination from first principles of the Curie or Néel temperature, has posed unanswered challenges for theorists until very recently. It is well known that the spin-flip excitation to the Stoner continuum costs too much energy and leads to an unphysically high critical temperature. Even in itinerant magnets, it is the orientational fluctuation of the local moments which governs the thermodynamic behaviors.[1] Yet the traditional empirical description of such an orientational variation, say, by the Heisenberg exchange model, has not been adequately combined with modern *ab initio* calculations, because this model expression holds exactly only in the weakly inhomogeneous limit.[2,3] Rigorous *ab initio* exchange parameters could only be defined under a small rotation with respect to a particular given spin configuration.[4] Therefore any single set of exchange parameters does not guarantee an exact description of thermodynamic behaviors and the phase transition bearing strong deviation from any given configuration. There remains the gap between the strongly restricted span in the *ab initio* calculation, on the one hand, and the paramount requirement in a meaningful statistical summation, on the other hand, over the spin configuration space.

Bridging this gap requires joint approaches of an appropriately defined *ab initio* description of the underlying interactions and a tractable statistical method. Staunton and Gyorffy[5] calculated the correlation between two spins in the paramagnetic (PM) state above T_C, and determined T_C by extrapolating the inverse susceptibility to zero. Sabiryanov *et al.*[6] calculated exchange integrals at the ferromagnetic (FM) limit, and determined T_C by Monte Carlo simulation for Fe and Co, and later also for Sm-(Fe,Co)-N.[7] The above two groups of work might be questioned in that the interaction involved in the *ab initio* calculation corresponds only to a particular (either PM or FM) state, which may not be appropriate for the strong fluctuation near the transition temperature. Essential progress was made recently by Uhl and Kubler. They defined and calculated the LSDA total energy surface $E(M,\vec{q},\theta)$ for SSDW configurations, and then the partition function was integrated over this configuration space in a mean field approximation. The Curie point was then determined for FM iron, cobalt, and nickel,[8] and also the Néel point for antiferromagnetic (AFM) fcc manganese.[9] Halilov *et al.*[10] used energy calculations over the same SSDW configuration space, but recast the energy into an expression in terms of wave-vector-dependent exchange integrals $J(\vec{q})$, and determined T_C of Fe and Ni in different, but also mean field, statistics. These two groups of work are the most highly regarded ones published on this subject so far, but their methods still suffer from the complexity of the large amount of energy calculations of the SSDW state and the uncertainty from adopting a mean field statistics. In contrast, Rosengaard and Johansson[11] used a more tractable approach, which determined exchange integrals by fitting to the linear muffin-tin orbital atomic-sphere approximation (LMTO-ASA) total energy of selected SSDW states, and T_C by the Monte Carlo (MC) simulation for bcc Fe, fcc Co, and Ni.

TABLE I. Total energy (relative to paramagnetic states) of fcc Fe ($a = 3.61$ Å) in a magnetic supercell structure of six monolayers along three crystallographic directions. The last column shows the range of variation of the self-consistent atomic moment value.

| Spin conf. | Total energy (mRy/cell) | | | Moment |
	$\langle 001 \rangle$	$\langle 110 \rangle$	$\langle 111 \rangle$	(μ_B/atom)
+ + + + + +	−7.57	−8.42	−8.50	2.49–2.52
+ + + + + −	−17.29	−18.27	−16.19	1.44–2.49
+ + + + − −	−27.20	−23.07	−19.27	1.50–2.23
+ + + − + −	−28.18	−25.17	−21.55	1.46–2.13
+ + − + + −	−33.37	−26.75	−23.83	1.13–2.02
+ + + − − −	−29.13	−24.36	−19.66	1.69–2.27
+ + − − + −	−32.04	−28.97	−21.92	1.60–1.91
+ − + − + −	−24.07	−24.01	−18.24	1.42–1.89

TABLE II. Magnetization energy and exchange integrals of fcc Fe ($a = 3.61$ Å) and Mn ($a = 3.89$ Å) in units of mRy, obtained by fitting to frozen collinear magnon states.

	fcc Fe	fcc Mn
E_M	4.523	22.898
J_1	−0.134 (−0.19)[a]	−0.733
J_2	0.191 (0.13)[a]	0.236
J_3	−0.022 (−0.03)[a]	−0.287
J_4	−0.084 (0.10)[a]	0.093
J_5	−0.006 (−0.04)[a]	0.045
J_6	−0.147	0.012
J_7	−0.003	−0.042
J_8	−0.010	−0.453
J_9	0.008	−0.016
J_{10}	0.005	0.012
J_{11}	−0.008	0.010

[a]Data obtained by direct calculation with respect to ferromagnetic state (Ref. 14).

The present work deals with AFM fcc Fe and Mn by adopting a method similar to Rosengaard and Johansson,[11] but in an even simpler version that the determination of the exchange integrals involves only a total energy calculation of frozen collinear magnon states. The results show that essential ingredients in the spin orientational fluctuation behavior could be captured even in this simple way, and the critical temperature T_N thus determined is in reasonable agreement with experiments.

The total energy was calculated for magnetic supercells consisting of six atomic layers in one period along $\langle 001 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions of the fcc lattice by use of the self-consistent linearized augmented plane-wave method with the von Barth–Hedin exchange-correlation term. Calculation details were given previously.[12] Considering the spin-flip and translational symmetry of the 2^6 spin configurations for each supercell system only eight are nonequivalent, and they are all realized through self-consistent solution of Kohn-Sham equation. The total energy is presented in Table I for fcc Fe. The FM states of the three supercells are physically equivalent; the small difference in their total energy (± 0.07 mRy/atom) is of numerical origin in the Brillouin zone sampling.

Data listed in Table I are used in a subsequent extraction of exchange interaction constants by a least squares fitting. For the present cubic case, the coupling is assumed of isotropic Heisenberg type and the exchange constants depend only on the distance. For simplicity and as an approximation, only a bilinear term is included in the present work, and other possible biquadratic and bicubic terms[11,13] are neglected in the present work. The single site magnetization energy E_M, which might be, in general, different for each spin and depends on the magnetization configuration, is found to be almost constant in a rather good approximation in the present range of moment variation (see Table I). Thus the total energy measured with respect to the PM state is written as

$$E_T = -\sum_i E_M - \sum_{i \neq j} J_{r(ij)} \vec{\sigma}_i \cdot \vec{\sigma}_j, \qquad (1)$$

where $\vec{\sigma}_i$ is the unit vector of the ith spin and $r(ij)$ identifies the distance between atom i and j to the radius of the rth

coordination sphere. Results obtained by least squares fitting are listed in Table II for both fcc Fe and Mn. Exchange parameters up to the sixth (for fcc Fe) or eighth (for fcc Mn) nearest neighbors are found to be important, showing a long-range and competing nature. The fitting error (0.22 and 0.6 mRy/atom for fcc Fe and Mn, respectively) is more than one order of magnitude less than the total energy variation (4.3 and 22.5 mRy/atom for fcc Fe and Mn, respectively). Thus the underlying interaction has been accounted for mostly.

To show the quality of the exchange integrals obtained according to above simple model and fitting procedure, a detail comparison is made to existing literatures for fcc Fe, while data for fcc Mn are scarce in previous publications. Since Eq. (1) is only an effective expression of the overall total energy change, the physical meaning of any single exchange constant could be obscure. Nevertheless, a comparison with Mryasov $et\ al.$[14] (also in Table II) is found also to be instructive, which is calculated with respect to the FM state and by use of a Green's function method. Our J_1, J_2, and J_3 values are in good agreement with their results in both sign and value (within error bars of $\pm 20\%$). The most prominent deviation is the negative J_4 and also the rather large negative J_6 value in the present calculation. Yet, as shown below, we found that the present results of negative J_4 and J_6 are essential in determining the energy dispersion of the SSDW, which is nevertheless in accordance with Refs. 14 and 15. So the deviation between the present effective interaction and that of Mryasov $et\ al.$ just serves as evidence showing that the exchange integrals are configuration dependent, and this dependence is more prominent for the long-range interaction.

By assuming the exchange is of Heisenberg type in Eq. (1), we have also extended the results obtained from the collinear spin states to cover the noncollinear spin configuration. A severe test of this assumption and the applicability of above effective exchange parameters would be afforded by comparing its results for the SSDW with the direct LSDA calculations given in the literature. Figure 1 plots the energy dispersion for SSDW obtained for fcc Fe from Eq. (1)
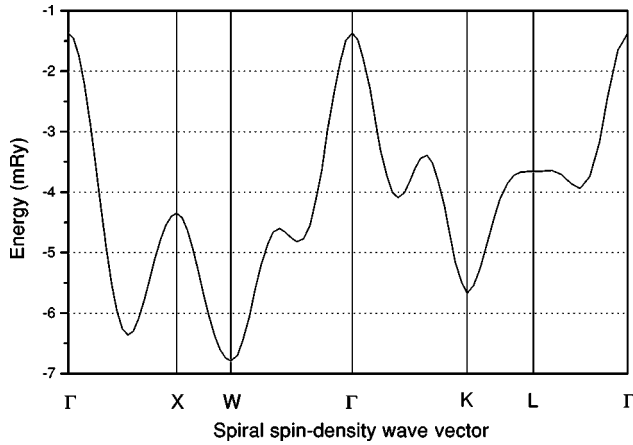
FIG. 1. Energy dispersion of the spiral spin-density wave obtained by the effective *ab initio* exchange model of fcc Fe ($a = 3.61$ Å).

FIG. 2. Temperature dependence of the energy correlation of fcc Fe ($a = 3.61$ Å) showing the phase transition at $T_N = 156 \pm 20$ K. Data are obtained for different cluster sizes (spin on each cube edge $n = 16, 24, 36$, or 50), and Monte Carlo steps per spin are 1000 (MC1k) or 3000 (MC3k).

and the effective *ab initio* exchange integrals listed in Table II. Along the line from Γ to X, there is an energy minimum at $\vec{q} = (0,0,0.56)2\pi/a$ in good agreement with the direct SSDW calculation which shows minimum at $\vec{q} = (0,0,0.6)2\pi/a$.[9,14,15] Along lines X-W-Γ, the curve in Fig. 1 is also in very good agreement with the direct SSDW energy calculation:[15] peaks and valleys exist at almost the same $\vec{q}$ positions. The dispersion curve from Γ to L agrees with Ref. 14 too. Note that present large negative J_4 and J_6 values are crucial in giving this correct energy dispersion. Neglecting them, or using the five exchange parameters calculated with respect to FM states (bracketed in Table II), gives a totally different dispersion: along line Γ-X-W-Γ only one minimum exists at the AFM state of $\vec{q} = (0,0,1)2\pi/a$, instead of the three minima and two maxima shown both in Fig. 1 and Ref. 15.

For fcc Fe, the present calculation gives a global minimum at the W point, though it is only 0.43 mRy lower than the energy at $\vec{q} = (0,0,0.56)2\pi/a$. A similar result was reported in Ref. 16, when the Wigner-Seitz sphere radius $S = 2.67$–2.72 a.u. (or $a = 3.616$–3.683 Å), but a different result was also reported previously by the same group of authors,[15] where the energy at W is 0.5 mRy higher than at $\vec{q} = (0,0,0.6)2\pi/a$ for $S = 2.67$ a.u. Besides, the amplitude of the energy variation given by the present calculation is somewhat smaller than that reported in Refs. 14 and 15,16. Even the energy difference between the collinear FM (Γ point) and AFM (X point) configuration of the present calculation (3.00 mRy) is also appreciably smaller. One reason for this difference might be due to the approximation used in both Refs. 14 and 15,16 that in those calculations, the spin-dependent potential has been included only inside the muffin-tin region, but neglected in the interstitial region. A comparison made by Korling and Ergon[17] showed that this does make a difference.

This SSDW ground configuration was also confirmed by another improved full potential calculation.[18] However, it has been questioned by a first principles spin dynamic calculation,[13] where in a calculation involving 32 atoms per cell, a simple $(0,0,q)$ SSDW was never found to be the most stable structure. Another molecular dynamics calculation
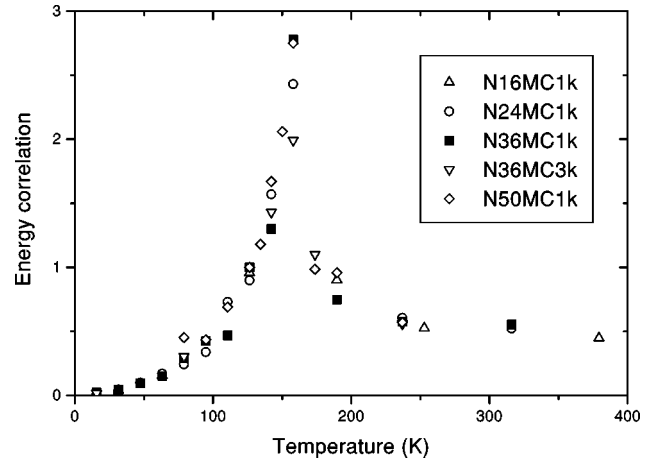
based on the Hubbard model[19] gave a SSDW ground structure with $\vec{q} = (0,1/3,2/3)2\pi/a$. None of the previous theoretical results were quite close to the experimental $\vec{q} = (0,1/11,1)2\pi/a$ state.[20] With the above effective *ab initio* Heisenberg exchange parameters, we carried out a MC search (more than 500 MC steps/spin). In order to avoid the influence of the periodic boundary condition, a search was made over large enough clusters consisting of n^3 (up to $n = 50$) atoms in the fcc lattice. The ground structure found is always exactly the SSDW energy at the W point, as long as the boundary condition permits (n equals multiples of 4). The exchange with a distance farther than the 11th neighbor, which has not been included in the present model fitting, is not likely strong enough to lead to the experimental ordering. Thus its physical origin might be beyond the reach of all these ideal model theoretical calculations.[18]

The effective J_r values obtained by fitting to the frozen magnon configurations are thus well justified. With these effective *ab initio* exchange integrals, a direct statistical approach to thermodynamic properties is computationally tractable, which does not rely on, and consequently is not limited by, other accompanying theoretical approximations, such as

TABLE III. Critical temperature T_N of fcc Fe ($a = 3.61$ Å or atomic volume $V = 11.76$ Å^3) and Mn ($a = 3.89$ Å or $V = 14.72$ Å^3).

	Reference	T_N (K)	Remarks
Mn	Calc. (present work)	383	cub.
	Calc. (Ref. 9)	446	cub.
	Expt. (Ref. 24)	490	alloy Mn(Fe,Cu,C) tet. $V = 12.96$ Å^3
Fe	Calc. (present work)	156	cub.
	Expt. (Ref. 20)	50	cluster in Cu
	Expt. (Ref. 21)	67	cluster in Cu
	Expt. (Ref. 22)	~ 200	film on Cu
	Expt. (Ref. 23)	~ 70	film on Cu

the mean field method. Here we present the results given by a standard MC simulation. The temperature dependence of the susceptibility shows a typical cusp manifesting the magnetic ordering, and even more prominently, the phase transition is shown in Fig. 2 by the temperature dependence of the energy correlation which is proportional to the product of the specific heat and temperature square. The Néel points determined from this MC simulation are listed in Table III. For fcc Fe, it is larger than the experimental values of the fcc Fe precipitates in Cu matrix,[20,21] but between the two values reported for epitaxial grown films on Cu.[22,23] For fcc Mn, the Néel point determined is lower than the experimental value[24] and the previous calculation.[9] A possible reason is the larger lattice constant used in the present calculation. Considering the complexity of the problem and the simplicity of the model used in the present calculation, the above results are in fact in reasonable agreement with the experiments and previous more sophisticated theory.

In summary, we have shown that fitting to the total energy of frozen collinear magnon states gives good effective *ab initio* exchange integrals. With the important long-range interactions included, the spin-orientation-dependent energy has been well expressed by this effective exchange model, as verified by a comparison with the direct LSDA calculation of the total energy of SSDW states. The thermodynamic behaviors and magnetic phase transition could be accessed in an *ab initio* manner with great simplicity, but with reasonable quantitative accuracy.

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