Oscillatory Curie Temperature of Two-Dimensional Ferromagnets

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The effective exchange interactions of magnetic overlayers Fe/Cu(001) and Co/Cu(001) covered by a Cu-cap layer of varying thickness were calculated in real space from first principles. The effective two-dimensional Heisenberg Hamiltonian was constructed and used to estimate magnon dispersion laws, spin-wave stiffness constants, and overlayer Curie temperatures within the mean-field and random-phase approximations. Overlayer Curie temperature oscillates as a function of the cap-layer thickness in a qualitative agreement with a recent experiment.

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The Curie temperature is one of the most important characteristics of ferromagnets. In particular, the Curie temperature of low-dimensional systems such as ultrathin films is of considerable interest. In a recent experimental study, Vollmer *et al.* [1] have shown that (i) the Curie temperature of fcc(001)-Fe ultrathin films on a Cu(001) substrate is considerably modified upon coverage by a Cu-cap layer, and (ii) that it varies in a nonmonotonous manner as a function of the Cu-cap-layer thickness, which indicates an oscillatory variation. An oscillatory behavior of the Curie temperature as a function of the spacer thickness was also found for fcc(001)-Co/Cu/Ni trilayers [2]. Such a behavior clearly cannot be explained within a localized picture of magnetism and calls for a first-principles theory of the Curie temperature in itinerant ferromagnets. In spite of considerable efforts in the past decades a first-principles calculation of the Curie temperature in the framework of itinerant magnetism, in particular, for low-dimensional systems, remains a very serious challenge.

One therefore has to rely upon some approximation schemes in order to calculate the Curie temperature of itinerant ferromagnets. A particularly simple and yet accurate approach consists of a mapping of the complicated itinerant electron system onto an effective Heisenberg model (EHM), $H = -\sum_{i \neq j} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j$, where $\mathbf{e}_i$ and $\mathbf{e}_j$ are the unit vectors of the magnetic moments at sites i and j, and the effective exchange interactions (EEIs) J_{ij} between any pair of magnetic moments are determined from first principles [3–9]. The thermodynamic properties of the ferromagnet including determination of the Curie temperature can then be calculated from the EHM by using statistical mechanical methods. A simple mean-field approximation (MFA) fails in many cases due to its neglect of collective excitations (spin waves), and more sophisticated approximations, such as the Green function method within the random phase approximation (GF-RPA) [10], are preferable. The success of this two-step approach relies upon the fact that it provides an almost exact description of low-lying magnetic excitations (spin waves) which give the largest contribution to the Curie temperature. On the other hand, this approach completely disregards longitudinal fluctuations of magnetic moments such as the Stoner excitations and it therefore is not suitable to describe ferromagnets with small exchange splitting such as, e.g., fcc-Ni, in which exist Stoner excitations with a rather low energy. We have recently applied this approach to bulk bcc-Fe, fcc-Co, and fcc-Ni and obtained a reasonable agreement with experimental Curie temperatures of Fe and Co, but not for Ni [9], similarly as in recent calculations based on the adiabatic spin-wave theory [4] or an alternative first-principles theory of spin fluctuations based on an idea of a generalized Onsager cavity field [11].

In the present paper we wish to calculate exchange interaction parameters, spin-wave stiffness constants, and Curie temperatures of two-dimensional monolayers of Fe and Co and, in particular, to investigate the influence of the substrate and of the cap layer. We find that (i) the exchange parameters, spin-wave stiffness constants, and Curie temperatures are strongly modified by the presence of a metallic substrate and/or a cap layer, and that (ii) they exhibit an oscillatory variation with the cap-layer thickness. This behavior is due to the Ruderman-Kittel-Kasuya-Yoshida (RKKY) character of exchange interactions in itinerant ferromagnets. Our results are in good qualitative agreement with the observations of Vollmer *et al.* [1] for which they provide the most natural explanation. The same theory can be used to interpret the experiment of Ney *et al.* [2], but the detailed analysis deserves a separate study.

The electronic structure of the system was determined in the framework of the first-principles tight-binding linear muffin-tin orbital method (TB-LMTO) generalized to surfaces [12]. In the framework of the magnetic force theorem [3,13], the expression for the EEIs between two sites i and j anywhere in the system is [3,14]

$$J_{ij} = \frac{1}{4\pi} \int_C \mathrm{Im}\, \mathrm{tr}_L \{\delta_i(z) g_{ij}^{\uparrow}(z) \delta_j(z) g_{ji}^{\downarrow}(z)\}\, dz\,. \quad (1)$$

Here tr_L denotes the trace over the angular momentum $L = (\ell m)$, $\delta_i(z) = P_i^{\uparrow}(z) - P_i^{\downarrow}(z)$, where $P_i^{\sigma}(z)$ are

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L-diagonal matrices of potential functions of the TB-LMTO method ($\sigma = \uparrow, \downarrow$), energy integration is performed in the upper half of the complex energy plane over a contour C starting below the bottom of the valence band and ending at the Fermi energy, and $g_{ij}^{\sigma}(z)$ are the site off-diagonal blocks of the system Green function corresponding to a given geometry. Possible lattice and/or layer relaxations at the overlayer are neglected. The intersite Green functions $g_{ij}^{\sigma}(z)$ can be evaluated either in the real space by using the cluster approach [3], the recursion method [8,15], or, as is done in the present paper and in Ref. [7], by the Bloch transformation which employs the two-dimensional translational symmetry of a given layer (for more details concerning the computational method, see Ref. [12]). We have calculated the EEI pairs J_{ij} up to 101 shells of the fcc(001) surface (i.e., up to the distance of about $10a$, where a is the lattice constant of the fcc lattice). Such a large number of the EEIs is needed, in particular, for an accurate estimate of the spin-wave stiffness constant in a real space, as is also known for the bulk case [9,14]. In actual calculations the sites i, j were limited to the magnetic layer, which is a good approximation in view of the smallness of the moments induced in the Cu. The spin-wave spectrum $E(\mathbf{q}_{\parallel})$, the spin-wave stiffness constant D, and the Curie temperatures T_c^{MFA} and T_c^{RPA} are expressed, respectively, in terms of the EEIs as follows:

$$E(\mathbf{q}_{\parallel}) = \frac{4\mu_{\mathrm{B}}}{M} \sum_{i \neq 0} J_{0i}[1 - \exp(i\mathbf{q}_{\parallel} \cdot \mathbf{R}_i)] + \Delta\,,$$

$$D = \frac{\mu_{\mathrm{B}}}{M} \sum_{i \neq 0} J_{0i} R_{0i}^2, \quad k_{\mathrm{B}} T_c^{\mathrm{MFA}} = \frac{2}{3} \sum_{i \neq 0} J_{0i}\,, \qquad (2)$$

$$\frac{1}{k_{\mathrm{B}} T_c^{\mathrm{RPA}}} = \frac{6\mu_{\mathrm{B}}}{M} \frac{1}{N_{\parallel}} \sum_{\mathbf{q}_{\parallel}} \frac{1}{E(\mathbf{q}_{\parallel})}\,.$$

Here, $N_{\parallel}$ is the number of sites per layer, the $\mathbf{q}_{\parallel}$ sum extends over the fcc(001) surface Brillouin zone, μ_B is the Bohr magneton, $R_{0i} = |\mathbf{R_0} - \mathbf{R_i}|$ is the interatomic distance, M is the magnetic moment per atom, and Δ is the magnetic anisotropy energy. It should be noted that T_c^{MFA} can be evaluated directly by using the one-site rotation term J_0 (expressed in terms of the site-diagonal element of the magnetic layer Green function similarly as its bulk counterpart [3,9]). The expression for T_c^{RPA} is a generalization of the bulk counterpart [10] to the case of magnetic layers: a vanishing T_c^{RPA} is obtained for $\Delta = 0$ [16] in agreement with the Mermin-Wagner theorem [17] and small relativistic effects have to be considered in order to obtain a nonvanishing value of T_c^{RPA}. The anisotropy energy Δ is taken here as an adjustable parameter. This is not a serious problem as the RPA Curie temperature has only a weak logarithmic dependence upon Δ [16], and it is thus sufficient to know the order of magnitude of Δ. The latter is typically of the order of the dipolar energy $2\pi M^2/V$, where V is the atomic volume. In calculations we used $\Delta_{\mathrm{Co}} = 0.052$ mRy and $\Delta_{\mathrm{Fe}} = 0.140$ mRy.

The evaluation of T_c^{RPA} is facilitated by the observation that it is proportional to the real part of the magnon Green function $G_m(z) = N_{\parallel}^{-1} \sum_{\mathbf{q}_{\parallel}} [z - E(\mathbf{q}_{\parallel})]^{-1}$ corresponding to a dispersion law $E(\mathbf{q}_{\parallel})$ and evaluated at $z = 0$. The corresponding $\mathbf{q}_{\parallel}$ summation is performed for complex energies from which the value at $z = 0$ is obtained by an analytic continuation technique [18]. The sum for the evaluation of the spin-wave stiffness constant is nonconvergent due to the RKKY character of magnetic interactions in metallic systems, and to overcome this difficulty we have calculated it by a regularization procedure [19] described in detail in Ref. [9].

The calculated EEIs for the first ten shells, magnetic moments, spin-wave stiffness constants, and the RPA and MFA Curie temperatures are summarized in Tables I and II for three limiting cases of magnetic Fe and Co layers, namely, the freestanding fcc(001) layer, the overlayer on the fcc-Cu(001) substrate, and the fcc(001) layer embedded in the fcc-Cu host.

TABLE I. Calculated values of effective exchange interactions for the first ten shells of fcc(001) Fe and Co magnetic layers: a freestanding (fs) layer, an overlayer (ov) on fcc(001)-Cu, and an embedded (em) layer in fcc-Cu. Numbers of atoms in a given shell and the corresponding shell radii (in units of lattice constants) are given in parentheses and square brackets, respectively. Corresponding values of magnetic moments M are also given.

	J_s(Co) [mRy]			J_s(Fe) [mRy]		
Shell	fs	ov	em	fs	ov	em
1 (4) [0.71]	2.85	2.34	2.01	3.40	2.69	2.62
2 (4) [1.00]	0.24	0.14	−0.12	0.12	0.22	0.39
3 (4) [1.41]	−0.02	−0.06	−0.01	−0.39	−0.37	−0.30
4 (8) [1.58]	−0.03	0.05	0.03	−0.23	−0.13	−0.05
5 (4) [2.00]	0.03	0.01	−0.01	0.05	0.03	0.04
6 (4) [2.12]	−0.01	−0.07	−0.07	−0.01	0.15	0.20
7 (8) [2.24]	−0.02	0.00	0.00	0.09	−0.03	−0.07
8 (8) [2.55]	0.00	0.00	0.00	0.01	0.04	0.03
9 (4) [2.83]	0.00	0.04	0.05	−0.03	−0.03	−0.01
10 (8) [2.92]	0.02	−0.02	−0.03	0.01	0.07	0.04
$M[\mu_B]$	2.22	1.79	1.57	3.06	2.82	2.59

TABLE II. Calculated values of the spin-wave stiffness coefficient D, T_c^{RPA}, and T_c^{MFA} for Fe and Co magnetic layers: a freestanding (fs) layer, and overlayer (ov) on fcc(001)-Cu, and an embedded (em) layer in fcc-Cu.

	D [meV · Å^2]		T_C^{RPA} [K]		T_C^{MFA} [K]	
	Fe	Co	Fe	Co	Fe	Co
fs	164 ± 4	570 ± 13	400	529	1265	1300
ov	331 ± 14	532 ± 9	515	426	1068	1043
em	462 ± 16	416 ± 8	612	324	1189	797

Concerning the EEIs, the following general conclusions can be drawn: (i) A pronounced dependence of magnetic moments on the coordination number is found, namely, their decrease with increasing number of nearest neighbors, the effect being stronger for the Fe layer; (ii) the EEIs are significantly enhanced (typically by a factor of 2 or more) as compared to their bulk counterparts; (iii) the EEIs depend strongly upon the presence of a substrate and a capping layer. The latter dependence is due to the RKKY character of the EEIs in metals: the coupling is not only mediated through the magnetic layer itself but also via the substrate and capping layer. This behavior is also clearly visible on the spin-wave spectra shown in Fig. 1 for Fe and on the exchange stiffness constant (Table II). We also present corresponding magnon densities of states (DOS) determined from the magnon Green function $G_m(z)$. A characteristic step of the height proportional to $1/D$ at the bottom of the magnon DOS accompanied by a pronounced van Hove singularity in the middle of the band are typical features of the two-dimensional bands with the nearest-neighbor interactions which are here only slightly modified by nonvanishing interactions in next shells. Interestingly, the spin-wave stiffness constants and Curie temperatures behave differently as a function of the atomic coordination for Co and Fe layers, i.e., for cases of the freestanding layer, the overlayer, and the embedded layer. This behavior can be related to the values of leading EEIs in both cases, in particular, to large antiferromagnetic couplings of 3rd and 4th nearest neighbors of Fe-based layers which effectively reduce the value of the spin-wave stiffness constant [see Eq. (2)], in particular, for the freestanding layer. On the contrary, the Co-based EEIs have the prevailing ferromagnetic character giving thus increasing spin-wave stiffness constants due to increasing values of the EEIs with reduced atomic coordination. The antiferromagnetic character of the EEIs for fcc-based Fe layers is strongly enhanced as compared to the bcc-Fe case [9] while the prevailing ferromagnetic character of the EEIs for bulk fcc-Co [9] and for fcc-Co layers remains unchanged.

The MFA Curie temperatures are typically of the same order magnitude as the corresponding bulk ones due to the fact that the reduced coordination is approximately compensated by the increase of the EEIs. This observation is in a strong disagreement with experimental data: this failure is due to the fact that the MFA violates the Mermin-Wagner theorem due to the neglect of collective transverse fluctuations (spin waves) and it is thus inappropriate for two-dimensional systems.

The RPA Curie temperatures as a function of the anisotropy energy Δ are shown in Fig. 2 for cases of the Co overlayer on fcc-Cu (001) and fcc-Co(001) layers embedded in Cu. The weak logarithmic dependence of T_c^{RPA} on Δ [16] is obvious: T_c^{RPA} varies by about 25% as Δ varies by an order of magnitude so that the results are not significantly influenced by our semiempirical choice of Δ. The RPA Curie temperatures are strongly reduced as compared to the corresponding bulk values thereby improving on the MFA results. Nevertheless, they are still too large as compared to observed Curie

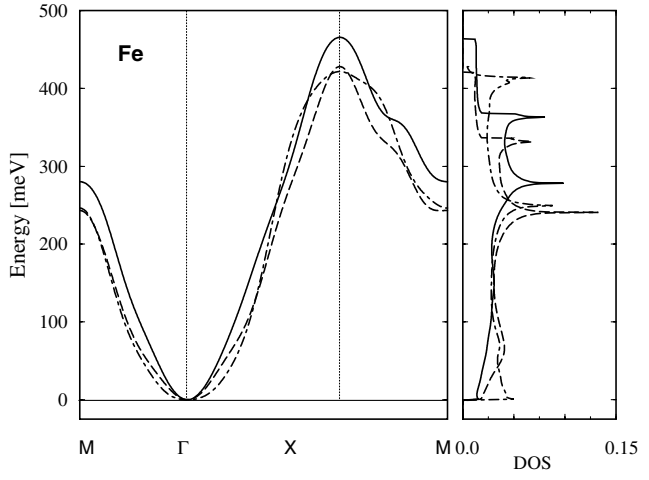

FIG. 1. Magnon dispersion laws (left frame) and corresponding densities of states [in states/(meV · atom)] for the Fe layer embedded in fcc-Cu (full line), Fe overlayer on fcc-Cu(001) (dashed line), and the freestanding Fe layer (dash-dotted line). We have set here $\Delta = 0$.

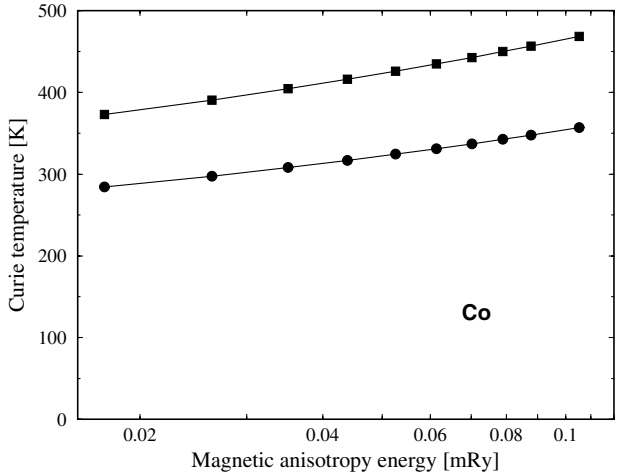

FIG. 2. RPA Curie temperatures of the Co overlayer on fcc-Cu(001) (full squares) and of the fcc(001)-Co layer embedded in fcc-Cu (full circles) as a function of the magnetic anisotropy energy Δ. Note the logarithmic scale on the abscissa.

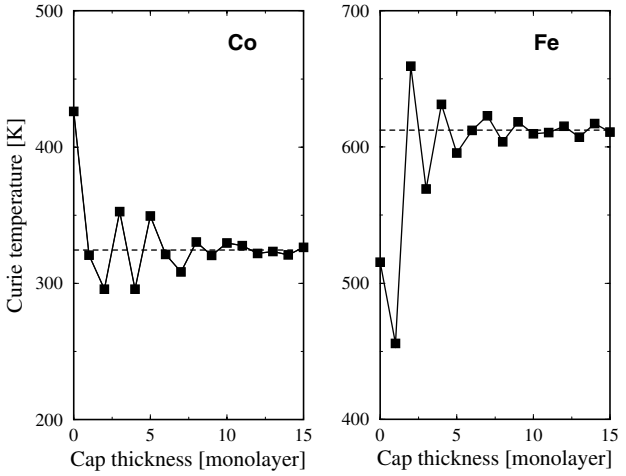

FIG. 3. T_c^{RPA} of Co (left) and Fe (right) overlayers on a fcc-Cu(001) substrate covered by a cap layer of varying thickness. The dashed lines represent the embedded layer limit (infinite cap thickness) while the limit of zero cap thickness corresponds to the uncovered overlayer.

temperatures of ferromagnetic monolayers (being of the order of 150–200 K). It is unclear whether this is due to some inaccuracy of the theory or to some imperfections of the samples used in the experiments. On the contrary, such important experimental facts as the strong influence of the metallic coverage on the Curie temperature [1] are well explained by our theory as illustrated in Fig. 3. The oscillatory character of T_c^{RPA} around the value corresponding to an infinite cap, i.e., to the limit of the embedded layer, is clearly visible and is in a qualitative agreement with the recent experiment of Vollmer *et al.* [1]. The origin of these oscillations can be traced back to the oscillatory behavior of the EEIs and it has the same origin as related oscillations of the interlayer exchange couplings found for the Co/Cu/Co(001) trilayer with a varying Cu-cap-layer thickness [20]. These oscillations are due to quantum-well states in the Cu-cap layer formed between the vacuum and the magnetic layer which, in turn, influence properties of the magnetic layer. We have verified that amplitudes of oscillations of the EEIs decay with the thickness d of the cap layer approximately as d^{-2}. The same thickness dependence was also found for the related case of the interlayer exchange interactions for the Co/Cu/Co trilayer with the varying thickness of the Cu-cap layer [21]. A similar behavior was also verified for the oscillatory dependences of T_c^{RPA} and T_c^{MFA} which, in turn, are derived from the EEIs. It should be noted that amplitudes and phases of oscillations can be influenced by the thickness of the magnetic layer and/or the presence of the disorder in the system.

In conclusion, in view of the interpretation proposed here, the oscillatory behavior of the Curie temperature of Fe films as a function of the Cu-cap thickness as reported by Vollmer *et al.* [1] would constitute the first *direct* experimental evidence of the oscillatory RKKY character of exchange interactions in itinerant ferromagnets.

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