The first-principles study of thermodynamical properties of random magnetic overlayers on fcc-Cu(001) substrate

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We present the theoretical study of thermodynamical properties of fcc-Cu(001) substrate covered by iron-cobalt monolayer as well as by incomplete iron layer. The effective two-dimensional Heisenberg Hamiltonian is constructed from first principles and properties of exchange interactions are investigated. The Curie temperatures are estimated using the Monte-Carlo (MC) simulations and compared with a simplified approach using the random-phase approximation (RPA) in connection with the virtual-crystal approach (VCA) to treat randomness in exchange integrals. Calculations indicate a weak maximum of the Curie temperature as a function of composition of the iron-cobalt monolayer. While a good quantitative agreement between RPA-VCA and MC was found for iron-cobalt monolayer, the RPA-VCA approach fails quantitatively for low coverage due to the magnetic percolation effect. We also present the study of the effect of alloy disorder on the shape of magnon spectra of random overlayers.

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I. INTRODUCTION

The Curie temperature is one of the most important characteristics of ferromagnetic materials. Its parameter-free determination for bulk ferromagnets and their alloys has progressed in the last decade. A reasonable agreement between calculated and experimental Curie temperatures was found for transition metal ferromagnets, some ordered and disordered transition metal alloys (e.g., Ni-based fcc-alloys), some f-metals (e.g., hcp-Gd, bcc-Eu), diluted magnetic semiconductors (e.g., GaMnAs) or Heusler alloys (see, e.g., a recent review). This progress was due to a combination of the first-principles determination of parameters of a (classical) Heisenberg Hamiltonian and its study using sophisticated statistical methods like, e.g., the random-phase approximation (RPA) or Monte-Carlo (MC) simulations. It should be noted, however, that there are magnetic systems for which the above approach has certain limitations or even fails. The present approach assumes the existence of robust moments and dominating effect of pair exchange interactions. Systems with induced moments, (e.g., FeRh), magnets with more complex than pair interactions, etc., are just few such cases, where the above approach is not successful. It is known that magnetic moments at system surfaces are enhanced due to the reduced number of nearest-neighbors, which is favorable for the validity of the Heisenberg model.

Determination of Curie temperatures $T_C$ of low-dimensional systems such as ultrathin films or even random magnetic monolayers deposited on non-magnetic substrates was studied very rarely in the past. Despite their importance. Regardless of considerable efforts in the past decade, the parameter-free determination of the Curie temperature of low-dimensional systems in the framework of itinerant magnetism remains a challenge for the theory. There are several reasons for this: (i) Already determination of the electronic structure of low-dimensional systems, in particular on the first-principles level, is much more demanding as compared to bulk systems, (ii) the presence of randomness in the system is another complication, (iii) the statistical treatment of the two-dimensional systems is much more delicate problem as compared to bulk systems because in two dimensions the interactions decay with the distance more slowly than in the bulk, and (iv) the presence of relativistic effects has to be taken into account for monolayers (the Mermin-Wagner theorem).

This paper is a natural extension of our previous study, in which the Curie temperature of two-dimensional systems was formulated for ideal, non-random systems based on exchange integrals determined from first-principles (specifically for Fe- and Co-overlayers on the fcc-Cu(001) substrate). Here we wish to extend this study to random overlayers. As case studies we consider (i) The random (Fe,Co)-overlayer deposited on the fcc(001) face of Cu, and (ii) The fcc-Cu(001) substrate with an incomplete coverage by iron atoms. One of aims of this study is a development of a reliable scheme for determination of $T_C$ which employs the MC method. This approach is accompanied by a simplified approach based on the RPA method in which randomness in exchange integrals is treated approximately in the virtual crystal approximation (VCA) and its reliability and limitations are tested. We also present the study of the effect of alloy disorder on the shape of magnon spectra of random (Fe,Co)-overlayers obtained by spin dynamics.

There are no experimental data for the present sys-
tem to compare with although FeCo-overlayers on various non-magnetic substrates (Cu,Pd,Rh) were studied often with the aim to estimate the magnetic anisotropy energies. Also, there are no doubts on the importance of a parameter-free approach to estimate $T_C$ of imperfect ultrathin magnetic overlays (see, e.g., a recent review).

II. FORMALISM

A. Electronic structure and Heisenberg model

The electronic structure of the system was determined in the framework of the Green function implementation of the scalar-relativistic tight-binding linear muffin-tin orbital method (TB-LMTO) in which the effect of the semi-infinite substrate was included properly in the framework of the surface Green function (SGF) approach while the disorder in the overlayers was treated in terms of the coherent potential approximation (CPA). The case of partial coverage of fcc-Cu(001) by iron atoms is simulated as a random overlayer consisting of iron atoms and vacancies described by empty spheres. The vacuum above the overlayer was simulated by empty spheres (ES). Electronic relaxations were allowed in four empty spheres adjoining the overlayer, the overlayer itself, and in five adjoining Cu substrate layers. This finite set of layers was sandwiched selfconsistently between a frozen semi-infinite fcc-Cu(001) and the semi-infinite vacuum including the effect of the dipole surface barrier. Possible small layer relaxations between substrate and overlayer were neglected although the present approach allows to include them.

We refer the reader for more details to Refs. 9,10.

An important advantage of the TB-LMTO-SGF approach is a possibility to estimate exchange interactions between magnetic atoms in the overlayer by a straightforward generalization of the well-approved bulk concept. The exchange integrals $J_{ij}^{Q,Q'}$ between sites $i,j$ occupied by atoms $Q$ and $Q'$ ($Q,Q'=\text{Fe,Cu}$ or $Q,Q'=\text{Fe,Cu}$) in the magnetic overlayer may be expressed as follows:

$$J_{ij}^{Q,Q'} = \frac{1}{4\pi} \text{Im} \int_{C} \text{tr}_{\delta} \left[ \delta^{Q}_{i}(z) \bar{g}^{\dagger}_{i,j}(z) \delta^{Q'}_{j}(z) \bar{g}^{\dagger}_{j,i}(z) \right] \text{d}z.$$  \hspace{1cm} (1)

Here, the trace extends over $s,p,d$-basis set, the quantities $\delta^{Q}_{i}$ are proportional to the calculated exchange splitting, and the (auxiliary) Green function $\bar{g}^{\dagger}_{i,j}$ describes the propagation of electrons of a given spin ($\sigma=\uparrow,\downarrow$) between sites $i,j$ in a random overlayer (the bar denotes the CPA configurational averaging). The integration path $C$ in the complex plane starts below the bottom of the valence band and ends at the Fermi energy. It should be noted that both the direct propagation of electrons in the random magnetic overlayer and the indirect one in the semi-infinite Cu-substrate are included in Eq. (1) on an equal footing. Finally, the disorder-induced vertex corrections due to the correlated motion of two electrons in a random overlayer can be neglected in a reasonable approximation due to the vertex-cancelation theorem.

Once the exchange interactions were known, we constructed a two-dimensional (2D) random classical Heisenberg Hamiltonian to describe the magnetic behavior of the random (Fe,X)-overlayer ($X=\text{Co},\text{vacancy}$) on a non-magnetic fcc-Cu(001) substrate

$$H = - \sum_{Q,Q'=\text{Fe,Cu}} \sum_{i,j \neq i} \eta_{i,j}^{Q,Q'} J_{ij}^{Q,Q'} \eta_{j,i}^{Q',Q} \mathbf{e}_{i} \cdot \mathbf{e}_{j} + \sum_{Q=\text{Fe,Cu}} \Delta^{Q} \sum_{i} (\eta_{i}^{Q})^{2} (\mathbf{e}_{i}^{z})^{2}. \hspace{1cm} (2)$$

In Eq. (2), $\mathbf{e}_{i}$ denotes a unit vector with the direction of the local magnetic moment at the site $i$ and $\eta_{i}^{Q}$ is the occupation index which equals 1 if the site $i$ is occupied by the atom $Q$ and zero otherwise. The second term is an uniaxial anisotropy of strength $\Delta^{Q}$ with an easy axis out of plane. By construction, the value of the corresponding magnetic moment is included in the definition of $J_{ij}^{Q,Q'}$, and positive (negative) values denote FM (AFM) couplings. Because exchange integrals for two-dimensional case decay with the distance $d$ between sites $i$ and $j$ more slowly as compared to the bulk, a large number of shells is needed to obtain well converged results, in particular for non-random cases of pure Fe- and Co-overlayers. Up to 90 shells were included in calculations of $T_C$ in the framework of the RPA and MC methods. The effect of small induced moments on substrate atoms was neglected (moments are of order few hundredths of $\mu_B$).

B. Statistical treatment

1. Random Phase Approximation

The expression for $T_C$ in the RPA is a generalization of its bulk counterpart to the case of random magnetic overlayers. (i) A vanishing $T_C$ is obtained in agreement with the Mermin-Wagner theorem for vanishing anisotropy energy $\Delta^{Q}$; (ii) The anisotropy energy is taken here as an adjustable parameter which we have identified with the dipolar energy and used the same values as in Ref. 2. This is not a serious problem as $T_C$ has only a weak logarithmic dependence on $\Delta^{Q}$, cf. Ref. 2 and (iii) We have averaged three exchange integrals $J_{ij}^{Q,Q'}$ ($Q,Q'=\text{Fe,Cu}$ or $Q,Q'=\text{Fe,vacancy}$) and introduced the effective non-random exchange integrals $J_{ij}^{\text{eff}}$ defined as

$$J_{ij}^{\text{eff}} = x^{2} J_{ij}^{\text{Fe,Fe}} + x(1-x)(J_{ij}^{\text{Fe,Cu}} + J_{ij}^{\text{Cu,vacancy}}) + (1-x)^{2} J_{ij}^{\text{X,X}} \hspace{1cm} (3)$$

which depend on the actual composition of random alloys Fe$_{x}$X$_{1-x}$ ($X=\text{Co,vacancy}$). This is the virtual-crystal approximation (VCA) and we have tested its applicability by performing MC simulations in which this approximation is not used (cf. Sec. III B). Using the VCA, the
Curie temperature is
\[
(k_B T_C^{\text{RPA}})^{-1} = \frac{3}{2N_\parallel} \sum_{q_\parallel} \left[ \Delta + J_{\text{eff}}(0) - J_{\text{eff}}(q_\parallel) \right]^{-1},
\]
where \(J_{\text{eff}}(q_\parallel)\) is the lattice Fourier transform of the effective exchange integrals \(J_{ij}\).

2. Monte Carlo simulation

In present work, we use the UppASD package\(^\text{31}\), developed at the Uppsala University for the study of magnetic materials. This package also contains MC code with the Metropolis algorithm which we utilized. The sampling in the Metropolis algorithm is controlled by the transition rate \(w(i,f)\) from an initial state \(i\) to a final state \(f\) which depends on energies \(E_i\) and \(E_f\) of an initial and a final state, respectively. The energies \(E_i\) and \(E_f\) were calculated using the Heisenberg Hamiltonian (2).

The number of trial moves in every Monte Carlo step (MCS) corresponds to the number of spins in the overlayer. The substrate is treated as rigid, adatoms do not diffuse, but rotation of spins of all adatoms is allowed. We start the simulation with a system of randomly distributed spin vectors in the overlayer. In the first phase of simulation, we only equilibrate the spin system; we use typically 10,000 MCS. After that, we perform the measurement of observable quantities; we measure over 50,000 MCS. We average calculated quantities over several independent runs. In the case of a random alloy, we employ several (typically 20) different random distributions of Fe and Co adatoms or Fe adatoms and vacancies in the overlayer.

One can use several methods for an estimation of the Curie temperature. We illustrate these possibilities in the case of a random (Fe,Co)-overlayer with the concentration \(x = 0.5\). One option is to employ the fourth–order size–dependent Binder cumulant\(^\text{14}\) \(U_L = 1 - \langle m_z^4 \rangle / \left[3 \langle m_z^2 \rangle^2 \right]\). Here, \(m_z\) is the \(z\)-component of the magnetization and \(L\) is the system size. This approach turned out to be quite useful in the past, though some limitations exist\(^\text{15}\). The shape of temperature dependence of the magnetization is influenced by the size \(L\). It leads often to the situation that cumulants for different system sizes cross in one point corresponding to the Curie temperature\(^\text{16}\). We calculated cumulants in our case, see Fig. 1. Unfortunately, we have found that the identification of a crossing point is not so clear as in the case of three dimensional systems.

Other methods are based on finding of a singularity point in the susceptibility \(\chi\) or in the specific heat \(C\). In the simulations, one can directly obtain only size-dependent quantities \(\chi_L\) or \(C_L\). One locates the temperature \(T^\chi_L\) or \(T^C_L\) of a local maximum of the susceptibility or specific heat for the size \(L\) and then performs extrapolation using corresponding scaling relation.

In this paper, we used mainly susceptibility (see Secs. III B and III C). After location a temperature \(T^\chi_L\) of a local maximum of the susceptibility for the size \(L\), we utilized the scaling relation
\[
T^\chi_L \approx T^\chi + \lambda L^{-\nu},
\]
where \(T^\chi\) is an estimate of Curie temperature for the infinite system. More specifically, the critical exponent \(\nu = 1\) for the two dimensional Heisenberg model with uniaxial anisotropy is known\(^\text{16}\). The system falls into the same universality class as the two-dimensional Ising model, for which all the critical exponents have analytically known values.

For the comparison with the method of cumulants, we evaluated \(T_C\) by the calculation of the size-dependent susceptibilities \(\chi_L\) for fcc (Fe,Co)/Cu(001) random overlayer with the concentration \(x = 0.5\) in Fig. 2. We carried out simulations for several system sizes (typically ranging from \(L = 16\) to \(L = 128\) and then we estimated \(T_C\) as an extrapolation of \(T^\chi_L\) using linear regression for infinite \(L\).

Similarly we calculate the size-dependent specific heat (figure is not presented).

C. Atomistic spin dynamics

Using the generalized Hamiltonian \(H\), Eq. (2), as a starting point, the temporal evolution of the atomic moments, \(\mathbf{m}_i\), where \(\mathbf{m}_i = |m_i| \mathbf{e}_i\) and \(|m_i|\) is the amplitude of the magnetic moment, at finite temperature is governed by Langevin dynamics through coupled stochastic differential equations of the Landau-Lifshitz form,
is controlled by the Gilbert damping parameter $\alpha$ is the dynamical structure factor and where the angular brackets denote an ensemble average approach is that it allows to address the dynamical properties we focus on are the space- and time-displaced correlation function, 

$$C_{ij}^\nu(t) = \langle m_i^\nu(t) m_j^\nu(0) \rangle - \langle m_i^\nu(t) \rangle \langle m_j^\nu(0) \rangle,$$

where the angular brackets denote an ensemble average and $\nu$ is the cartesian component. Its Fourier transform is the dynamical structure factor

$$S_{ij}^\nu(q, \omega) = \frac{1}{\sqrt{2\pi}N} \sum_{ijkl} e^{iq(q_i - q_j)} \int_{-\infty}^{\infty} e^{i\omega t} C_{ij}^\nu(t) dt,$$

where $q$ and $\omega$ are the momentum and energy transfer, respectively. $S(q, \omega)$ is the quantity probed in neutron scattering experiments of bulk systems, and can analogously be applied to spin-polarized electron energy loss spectroscopy (SPEELS) measurements. By plotting the peak positions of the structure factor along particular directions in reciprocal space, the magnon dispersions may be obtained.

### III. RESULTS

#### A. Exchange interactions

In this section we wish to illustrate some general features of exchange interactions for 2D systems. We shall start with the study of the dependence of exchange integrals $J^{Fe,Fe}_{ij}$ on the distance between Fe atoms in the fcc(001) monolayer along the direction [1,1] in various cases, namely (i) The isolated (unsupported) Fe-layer, (ii) The Fe-overlayer on fcc-Cu(001), and (iii) The random (Fe$_{0.5}$,Co$_{0.5}$)-overlayer on fcc-Cu(001). In this way we can study the effect of indirect interactions of Fe-atoms via the substrate (missing for unsupported layer) as well as the effect of disorder. The case of unsupported Fe-layer was studied using the same model in which, however, the iron overlayer was separated from the substrate by eight layers of empty spheres from the fcc-Cu(001) substrate. It is well-known that the exchange integrals in bulk ferromagnets decay with distance $d$ as $d^{-3}$. It is seen from Fig. 3b that for the unsupported layer the decay with distance is much slower, namely, proportional to $d^{-2}$.

The effect of the substrate is striking as illustrated in Fig. 3b for Fe-overlayer on fcc-Cu(001). The decay of exchange interactions with distance $d$ is approximately $d^{-2.5}$ as a result of interactions via the substrate. Also illustrated in Fig. 3b is the additional exponential decay of exchange interactions due to the alloy disorder for the case of (Fe$_{0.5}$,Co$_{0.5}$) overlayer on the substrate.

The exchange integrals for pure Fe and Co overlayers on fcc-Cu(001) substrate are shown in Fig. 4b. We observe generally larger values of exchange integrals for the iron overlayer as compared to a cobalt one indicating a higher Curie temperature in the former case. Also shown are configurationally averaged integrals $J_{ij}^{Q, Q'}$, $Q, Q'$=Fe,Co for (Fe$_{0.5}$,Co$_{0.5}$) overlayer (for VCA values, see Eq. (3)) used in an approximate treatment of the Curie temperature (see below). It is interesting to note that these effective integrals are similar to the species resolved $J_{ij}^{Fe,Co}$ integrals shown in Fig. 4b.

Species-resolved exchange integrals for equiconcentration coverage of fcc-Cu(001) substrate by iron and cobalt atoms are shown in Fig. 4b. The remarkable feature is a relative similarity of all three kinds of exchange integrals which is an indication of the validity of a simplified VCA treatment as discussed below.

Finally, in Fig. 5 we show the dependence of exchange integrals $J_{ij}^{Fe,Fe}$ on the coverage $x$ of the fcc-Cu(001) surface by iron atoms. The exchange integrals increase with decreasing coverage. The reason is their impurity char-
B. Curie temperature: iron-cobalt overlayer

We have first investigated the magnetic properties of random Fe\textsubscript{1-x}Co\textsubscript{x} overlayer on Cu substrate using two methods: the RPA and the MC simulation. In MC simulation we calculated the size-dependent susceptibility and then performed extrapolation as described in the subsection 11B2. As discussed above, in the RPA we used an approximate VCA while MC simulations were done both for the VCA as well as for the realistic case with three different exchange integrals \( J_{ij}^{Q,Q'}(Q,Q' = \text{Fe,Co}) \). The RPA-VCA approximation was used successfully for the calculation of \( T_C \) of bulk Ni-rich transition metal alloys\(^{21}\). In Ref\(^{22}\), it was demonstrated numerically on a simple model that VCA is a good approximation above the percolation limit and for extended exchange integrals. Another reason for validity of the RPA-VCA in this case is a similarity of exchange integrals \( J_{ij}^{Q,Q'}(Q,Q' = \text{Fe,Co}) \) as shown above. On the contrary, for localized exchange integrals and a very low concentration of magnetic impurities the VCA fails, like, e.g., in (Ga,Mn)As and (Ga,Mn)N diluted semiconductor alloys\(^{22}\). In the present case one should expect that the VCA will be a good approximation because of extended character of exchange integrals \( J_{ij}^{Q,Q'} \) and their similarity for various atom types as indicated above.

The calculation confirms this prediction as it is obvious from Fig. 6 in which we compare \( T_C \) of fcc-(Fe,Co)/Cu(001) random overlayer over the whole concentration range. In the limit of Fe- and Co-overlayer on fcc-Cu(001) the present results agree well with a previous study\(^{23}\) and small differences are due to the differences in technical details. We have obtained well-pronounced maximum in the concentration dependence of \( T_C \), which...
FIG. 5: The Fe-Fe exchange integrals as a function of the shell distance for three different coverages of fcc-Cu(001) surface by Fe atoms, indicated in the plot.

FIG. 6: (Color online) Concentration dependence of $T_C$ for fcc (Fe,Co)/Cu(001) random overlayer as a function of Co-concentration. Lower panel: We compare the MC simulations using random exchange integrals (circles) with the simplified MC-VCA (diamonds) and RPA-VCA (triangles and squares). In the VCA cases, we employ non-random alloy with effective concentration-dependent exchange integrals (see the text). Also shown is the RPA-VCA result for reduced anisotropy (see the text). Upper panel shows mean field approximation.

reminds a similar maximum in the concentration trend of random bulk FeCo alloys in the concentration range in which the bcc-phase exists. The calculated $T_C$ depends on the values of the anisotropy energy $\Delta$ of constituent atoms, although such dependence is quite weak as demonstrated in Ref. 2. We remind that this term is responsible for the formation of a narrow gap in the spin-wave spectra which is an origin of the finite Curie temperature for the monolayer case. Due to this term the Curie temperature determined in the framework of the RPA or Monte Carlo is much lower than its mean-field counterpart as it is obvious from Fig. 6 (see also Ref. 3). A reliable choice of this term is a problem. In the present case we have chosen the same values as in Ref. 2 ($\Delta_{Fe}=0.140$ mRy $\Delta_{Co}=0.052$ mRy) and their average in the VCA models in order to have a direct comparison with the case of ideal overlayers. A recent study indicates that this value may be significantly smaller. Because of this uncertainty, we have tested the robustness of the present result with respect to various values of this term using the RPA-VCA method. In particular, we show in Fig. 6 results of the RPA-VCA for the case in which we used the same values of $\Delta$ for both Fe and Co, but reduced by an order of magnitude as compared to that for Fe-atoms ($\Delta=0.015$ mRy). Calculated Curie temperatures are lowered in agreement with the previous study, but the concentration maximum, although less pronounced due to the same values of $\Delta$, is still present. It should be noted that a reliable experimental estimate of the Curie temperature of monolayers is still a challenge.

We note that similar maxima in the concentration trend of $T_C$ exist in random bulk bcc-FeCo and fcc-NiFe alloys. In the former case the total moment has a weak maximum for about 30% of Co, in the latter case the total moment varies almost linearly with the content similarly like in the present overlayer case. This means that there is no simple relation between concentration trends of total moments and Curie temperatures. The Curie temperature is determined by the exchange integrals. It should be noted that a discussed concentration maximum of $T_C$ is seen already in their mean-field values, Fig. 6 which, in turn, are directly proportional to the sum of averaged exchange integrals, Eq. 3. This can be considered as a precursor of the concentration maximum of $T_C$.

We can conclude that a critical comparison of calculated Curie temperatures of random magnetic overlayers on nonmagnetic substrates can be conveniently performed using a simplified RPA-VCA approach which is significantly more numerically efficient than MC simulations. This is mostly due to the fact that exchange integrals for various species are rather similar. Using the fast RPA-VCA approach we have verified that due to a
slow decay of exchange integrals with distance one should carefully check the convergence of results with the number of shells included in simulations.

C. Curie temperature: incomplete coverage by iron

The next case is the model of partial coverage of the fcc-Cu(001) substrate by iron atoms. In this case, contrary to the previous model of (Fe,Co)-overlayer, the only non-zero exchange integrals are those among Fe atoms. The effective exchange integral (VCA) is thus \( J_{ij}^{\text{eff}} = x^2 J_{ij}^{\text{Fe-Fe}} \), where \( x \) denotes the coverage (\( x=1 \) corresponds to ideal Fe-overlayer). It should be noted that for 2D-systems the effect of percolation may lead to reduction of Curie temperature to zero value. In particular, it is known that the site percolation threshold for the square lattice with interaction up to next nearest neighbors is \( p_c \approx 0.592 \) and that the percolation threshold may progressively decrease with the range of interaction\(^\text{26} \) provided the strength of interaction is independent of a range of neighbor bonds. Despite the fact that exchange integrals are relatively long-ranged, one thus should expect that the VCA will represent a substantial approximation, at least at low coverages.

We have estimated the Curie temperature of fcc-Fe\(_x\)/Cu(001) system for coverages \( x=1, 0.75, 0.5, \) and \( 0.25 \). The results are summarized in the Table 1. Both the RPA-VCA and MC simulations give qualitatively the same result, namely, an almost linear decrease of the Curie temperature with decreasing coverage. On the other hand, the RPA-VCA overestimates the Curie temperature with decreasing coverage as expected and for very low coverage (\( x=0.25 \)) it gives even the qualitatively incorrect result as the MC leads to a collapse of the long-range magnetic order. One can thus conclude that for systems with very different exchange integrals one should be careful when using simplified approaches like the RPA-VCA. Another example of such system can be, e.g., the surface alloy fcc-(Cu,Mn)/Cu(001) with negligible exchange integrals between Cu atoms and also between Cu and Mn atoms due to a negligible magnetization of Cu atoms. On the other hand, the 2D-generalization of the random RPA approach\(^\text{27} \) which was successfully applied to the diluted magnetic semiconductors can be a fast and reliable counterpart to the numerically demanding MC simulations which, on the other hand, are the most reliable.

D. Magnon spectra

Progress in experimental techniques in the recent years has made it possible to measure magnon dispersion even in ultrathin magnetic overlayers, such as a single Fe monolayer on W(110), using spin-polarized electron energy loss spectroscopy (SPEELS) measurements\(^\text{28} \). Although the present random iron-cobalt overlayer has not yet been measured, our calculations hopefully could motivate such a study. In principle, there are at least three sources of broadening of the magnon dispersion, namely, the alloy disorder, the transversal temperature fluctuations of the magnetic moments originating from the coupled thermal bath, and the longitudinal Stoner excitations. At present, the ASD formalism does not include Stoner excitations, but for low temperatures and smaller wavevectors, the density of magnons dominates over Stoner excitations. Here, we focus on the broadening originating from alloy disorder by calculating magnon dispersions for the following cases (i) pure Fe, (ii) Fe\(_{50}\)Co\(_{50}\), and (iii) Fe\(_{75}\)Vac\(_{25}\) overlayer on top of Cu(001), as displayed in Fig\(^\text{27}\). The color is a measure of magnon damping (the full width at half maximum of the magnon spectral function). In all three cases, the temperature is fixed at \( T=5\)K and \( \alpha=0.005 \). We probe magnons in the fcc(001) two-dimensional Brillouin zone by following the path \( \bar{X}-\bar{\Gamma}-\bar{M}-\bar{X} \). The \( \bar{X} \) and \( \bar{M} \) points correspond to \( p(2\times1) \) and \( c(2\times2) \) antiferromagnetic structures, respectively.

The magnon spectra for the Fe overlayer show very little broadening throughout the Brillouin zone as expected, since there is no alloy disorder in this case. Alloying Fe with Co changes the situation. Here the spectra are more diffuse due to the alloy disorder. It is worth noting that the broadening is most pronounced around the \( \bar{M} \) point in the Brillouin zone. The higher frequencies at the \( \bar{X} \) and \( \bar{M} \) points are consistent with the higher \( T_C \) found in Fe\(_{0.5}\)Co\(_{0.5}\) overlayer as compared with the pure Fe case. The difference between magnetic properties of Fe and Co atoms is not very big and there are still distinct magnon excitations visible in the whole BZ. However, an extreme situation is encountered in the dilute case (Fe\(_{75}\)Vac\(_{25}\) alloy). Here the alloy disorder is large causing a very diffuse magnon spectra. A similar result has been found in three–dimensional diluted magnets by random phase approximation\(^\text{28} \). One can say that magnon excitations in this case are strongly damped and existing only for small wave vectors, i.e., for longwave magnons which are less sensitive to local site disorder. In this incomplete Fe coverage (\( x=0.75 \), we observe a dispersionless excitation with the energy close to zero. It corresponds to localized magnons that appear close and below the percolation threshold. This phenomenon was discussed by Chakraborty and Bouzerar\(^\text{29} \) in a three–dimensional case, but the same arguments are valid also in two-di-

| \( x \) | \( T_C^{\text{MC}} (K) \) | \( T_C^{\text{RPA}} (K) \) |
|---|---|---|
| 1.0 | 552 | 552 |
| 0.75 | 361 | 415 |
| 0.5 | 140 | 269 |
| 0.25 | – | 131 |
FIG. 7: (Color online) Magnon spectra for Fe/Cu(001) (upper panel), (Fe_{0.50},Co_{0.50})/Cu(001) (middle panel) and (Fe_{0.75},Vac_{0.25})/Cu(001) (lower panel) evaluated at $T = 5$ K, and for $\alpha=0.005$.

IV. DISCUSSION AND CONCLUSION

We have presented the first-principles theory of thermodynamical properties of random magnetic overlayers on non-magnetic metallic substrates and applied it to two systems, namely, to a random iron-cobalt monolayer on the fcc-Cu(001) substrate and to the case of partial coverage of fcc-(001) face of copper by iron atoms. Atomistic spin dynamics simulations were used to predict magnon dispersions in random overlayers, where broadening from alloy disorder was quantified.

The main conclusions from our study are: (i) The exchange integrals of magnetic overlayers decay more slowly as compared to the bulk cases and large number of shells has to be included in the statistical treatment to obtain well converged result; (ii) Contrary to the bulk case, we have found that the most efficient and reliable approach to estimate the Curie temperature of magnetic overlayers is the estimate of the susceptibility combined with the scaling relation rather than the cumulant method; (iii) The simplified, but numerically efficient RPA-VCA approach was tested and limits of its applicability were established. It was found that the RPA-VCA is applicable for systems with similar exchange integrals (like, e.g., FeCo-overlayer), but it fails for systems with very different values of exchange integrals (like, e.g., incomplete Fe-overlayer); (iv) Calculations indicate the presence of a maximum in the concentration dependence of the Curie temperature similar to that observed in bulk bcc-FeCo alloys.

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