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Magnetism-induced ordering in two and three dimensions

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A first-principles theory of alloy ordering in two and three dimensions in the presence of ferromagnetism is described. Using the generalized perturbation method, the order-disorder transition from the bcc $Fe_{50}Co_{50}$ random alloy into the ordered CsCl-structure FeCo alloy and its ordering temperature are found to agree reasonably well with available experimental data. A similar ordering tendency for the formation of the ordered $c(2\times 2)$ phase of the $Fe_{50}Co_{50}$ surface alloy on fcc Cu(001) is investigated.

Most technologically important alloys involve elements from the end of the 3d transition metal series. Recent progress in the controlled deposition of metallic layers has led to a number of novel phenomena, such as oscillations in the exchange coupling between ferromagnetic layers separated by nonmagnetic spacer layers. The description of such systems in terms of physically meaningful parameters and their prediction from the electronic structure are thus of great importance.

In the present paper we investigate the ordering of the bcc $Fe_{50}Co_{50}$ alloy, and show that the experimentally observed CsCl ($B2$) superstructure arises from the presence of ferromagnetism in this system. A similar ordering tendency is found also for a two-dimensional analog, namely, for the formation of the ordered $c(2\times 2)$ phase of the $Fe_{50}Co_{50}$ surface alloy on Cu(001).

The ordering in bulk alloys as induced by the presence of magnetic moments was predicted theoretically by Gautier[1] and Ducastelle[2] using the generalized perturbation method[3] (GPM) as developed within the framework of the empirical tight-binding method. A first-principles description of the magnetic and compositional order in bulk alloys based on local spin-density approximation (LSDA) calculations appeared only recently.[4,5] This description is based on a mean-field study of magnetic and concentration fluctuations within the framework of the Korringa-Kohn-Rostoker coherent potential approximation (KKR-CPA) method and was applied to the cases of Fe-rich FeV alloys[4] and Ni-rich fcc NiFe alloys.[5]

The present approach consists of two steps: (i) the determination of the self-consistent electronic structure of a random bulk alloy and of a semi-infinite substrate with a random overlayer of the corresponding composition within the LSDA; (ii) a study of the instability of these disordered phases with respect to the formation of ordered superstructures by using the static concentration wave method[6] as described by the GPM, and its generalization to surfaces.[7] The *ab initio* nonmagnetic versions of the GPM for bulk systems and surfaces are discussed in Refs. 8 and 9, respectively.

In the present study the bulk and surface electronic structure in the presence of chemical disorder is described by the tight-binding linear muffin-tin orbital (TB-LMTO) method within the framework of the CPA,[10,11] as generalized to collinear spin structures.[12] In the overlayer case the multipole expansion of the nonspherical charge densities[13] is included in order to account properly for the potential barrier across the surface (for further details see Refs. 10–12).

We shall first discuss the effect of magnetism-induced ordering qualitatively[1,2] by relating the ordering energy to the corresponding change in the spin-projected band energy of the ferromagnetic bulk and/or surface alloy. The simple dependence on the spin index σ ($\sigma=\uparrow,\downarrow$) is a consequence of the present limitation to systems with a collinear spin structure. This in turn corresponds to a complete neglect of the disordered local moments and is thus inappropriate for the paramagnetic state. In the case of the bcc FeCo system, where the order-disorder transition from the bcc to the CsCl structure occurs below the Curie temperature,[14] the present approach, however, gives a reasonable quantitative description of the interatomic interactions in the presence of magnetic moments.

The effective pair interactions $V_{\mathbf{R},\mathbf{R}'}$ between two sites $\mathbf{R}$ and $\mathbf{R}'$ are determined as the sum of the corresponding two spin-polarized terms $V^{\sigma}_{\mathbf{R},\mathbf{R}'}$, $V_{\mathbf{R},\mathbf{R}'} = V^{\uparrow}_{\mathbf{R},\mathbf{R}'} + V^{\downarrow}_{\mathbf{R},\mathbf{R}'}$. The bcc $Fe_{50}Co_{50}$ alloy is a strong ferromagnet,[12] and thus pair interactions connected with the completely filled majority subband are very small.[3] The ferromagnetic alloy orders because the minority spin subband is less filled than in the paramagnetic state giving thus positive first nearest-neighbor interactions which stabilize the CsCl structure. The effective pair interactions (see below) depend strongly on the chemical disorder and the band filling. Consequently, the phase stability of random alloy is strongly modified by the ferromagnetism.

The central quantity of the GPM, the effective pairwise interchange interaction in a random alloy $A_{1-x}B_x$,

$$V_{\mathbf{R},\mathbf{R}'} = \sum_{\sigma} \left(V^{\sigma,AA}_{\mathbf{R},\mathbf{R}'} + V^{\sigma,BB}_{\mathbf{R},\mathbf{R}'} - V^{\sigma,AB}_{\mathbf{R},\mathbf{R}'} - V^{\sigma,BA}_{\mathbf{R},\mathbf{R}'} \right), \quad (1)$$

is defined in terms of effective pair interactions at the sites $\mathbf{R}$ and $\mathbf{R}'$, $V^{\sigma,QQ'}_{\mathbf{R},\mathbf{R}'}$, $(Q,Q' = A,B)$,

$$V^{\sigma,QQ'}_{\mathbf{R},\mathbf{R}'} \equiv v^{\sigma,QQ'}_{\mathbf{R},\mathbf{R}'}(E_F)\,,$$

$$v^{\sigma,QQ'}_{\mathbf{R},\mathbf{R}'}(E) = \frac{1}{\pi}\mathrm{Im}\int_{E_b}^{E} \mathrm{tr}\,[t^{\sigma,Q}_{\mathbf{R}}(z)\bar{g}^{\sigma}_{\mathbf{R},\mathbf{R}'}(z)t^{\sigma,Q'}_{\mathbf{R}'} \times(z)\bar{g}^{\sigma}_{\mathbf{R}',\mathbf{R}}(z)]_{z=\eta-i0}\,d\eta\,. \quad (2)$$

Here, $t^{\sigma,Q}(z)$ is the on-site T matrix,[10,11] the trace is confined to the orbital momentum space, and E_F and E_b denote the Fermi energy of the system (bulk alloy or the nonmagnetic substrate) and the corresponding valence band bottom, respectively. In (2) the $\bar{g}^{\sigma}_{\mathbf{R},\mathbf{R}'}(z)$ are the so-called site off-diagonal elements of the configurationally averaged Green's function.[10–12] The Fourier transform $V(\mathbf{k})$ of $V_{\mathbf{R},\mathbf{R}'}$, Eqs. (1),(2), where $\mathbf{k}$ is a vector of the corresponding bulk (bcc) or surface [fcc(001)] Brillouin zone, is directly related to the stability of the random phase with respect to the ordered phase. An absolute minimum of $V(\mathbf{k})$ at $\mathbf{k} = \mathbf{0}$ indicates a tendency of phase separation, while absolute minima at various high-symmetry points $\mathbf{k}$ indicate an ordering tendency to form a superstructure compatible with the vector $\mathbf{k}$.[6,7,15] The value of the absolute minimum gives a reasonable effective-medium estimate of the transition temperature in a random alloy $A_{1-x}B_x$, namely,

$$T^{\mathrm{ord}} = -x(1-x)V(\mathbf{k})/k_B\,, \quad (3)$$

where x is the concentration of B species. This analysis can also be applied to the case of a disordered overlayer.[7]

The effective-medium estimate of T^{ord} can be improved by using more advanced statistical methods, namely, either the cluster-variation method[16] (CVM) or Monte-Carlo simulations.[17] This applies in particular to the surface case where due to the reduced translational symmetry an effective-medium estimate of the ordering temperature is less justified. In the present pa-

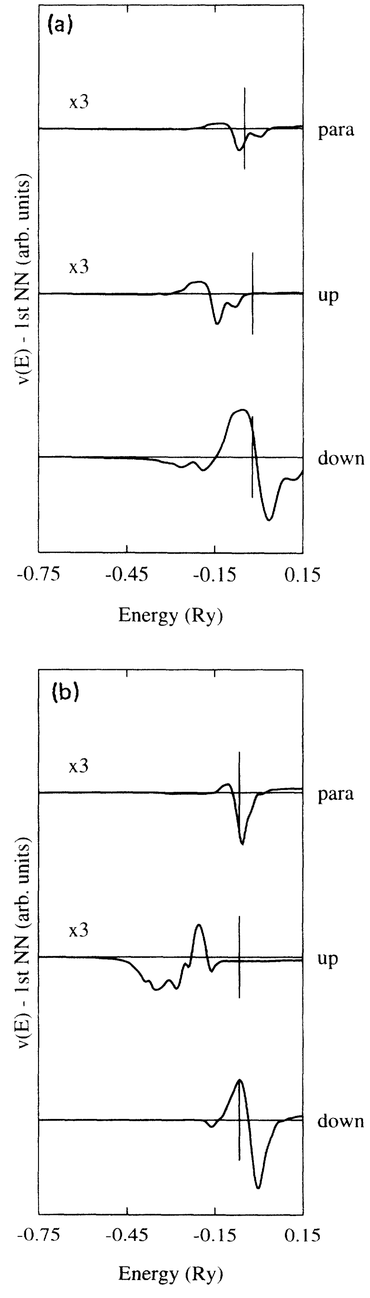

FIG. 1. Energy-resolved pairwise interactions $v_1(E)$ for the first nearest neighbors in the nonmagnetic state, and for the up (majority) and the down (minority) subbands in the ferromagnetic state: (a) bulk bcc $Fe_{50}Co_{50}$ random alloy and (b) $Fe_{50}Co_{50}$ random overlayer on a Cu(001) substrate. The vertical lines denote the positions of the Fermi level E_F in the bulk alloy (different for the nonmagnetic and magnetic cases) or in the overlayer case (determined by the bulk Cu substrate).

per the Monte Carlo method is applied to an effective Ising Hamiltonian as derived from first-principles electronic structure calculations within the bulk GPM (Ref. 8) and its generalization to the surface case,[7,9] restricted to collinear spin structures (1).

The computational details of the electronic structure part of the problem are the same as in Ref. 12. The site off-diagonal elements of the bulk and overlayer Green's functions $\bar{g}^{\sigma}_{\mathbf{R},\mathbf{R}'}(z)$ are calculated by integrating over the corresponding full Brillouin zone. We have calculated all pairwise interchange interactions up to the 11th shell of neighbors in real space. The quantity $V(\mathbf{k})$ was calculated by a Fourier transform assuming that the $V_{\mathbf{R},\mathbf{R}'}$ are well converged up to the 11th shell. For the purpose of illustration we have also calculated in direct analogy to (1) the energy-resolved pairwise interchange interactions $v_{\mathbf{R},\mathbf{R}'}(E)$ defined in terms of $v^{\sigma,QQ'}_{\mathbf{R},\mathbf{R}'}(E)$, Eq. (2).

We found a pronounced minimum of $V(\mathbf{k})$ for $\mathbf{k} = \frac{2\pi}{a}(1,1,1)$ in the case of the bulk bcc $\mathrm{Fe}_{50}\mathrm{Co}_{50}$ alloy, which in agreement with experiment[14] clearly indicates an ordering tendency into the ordered CsCl structure. For the dominating first nearest-neighbor shell the energy-resolved quantities $v_1(E)$ in the nonmagnetic state and for the up (majority) and down (minority) electrons in the random ferromagnetic alloy (see Fig. 1) clearly support a simple tight-binding picture of magnetism-induced ordering as proposed in Refs. 1, 2: In the absence of magnetic moments the negative value of $v_1(E_F)$ indicates segregation rather than an ordering tendency. Since the majority electrons in a completely filled band do not participate in the ordering phenomena, the ordering tendency is due to the less-filled minority electrons bands. It should be noted that this mechanism does not exclude other mechanisms, e.g., the possible influence of fluctuating magnetic moments in the paramagnetic disordered local moment state, which however is beyond the scope of the present paper.

We performed a similar study also for the case of an FeCo overlayer on a Cu(001) substrate and found a minimum of $V(\mathbf{k}_{\parallel})$ for $\mathbf{k}_{\parallel} = \frac{2\pi}{a}(1,0)$, which in turn corresponds to the formation of an ordered $c(2\times 2)$ superstructure for a random $\mathrm{Fe}_{50}\mathrm{Co}_{50}$ overlayer on a Cu(001) nonmagnetic substrate. A similar ordering tendency was found experimentally and explained theoretically[7] in the case of a paramagnetic CuPd surface alloy on a Cu(001) substrate. The underlying ordering mechanism is the same as in the bulk case since the FeCo overlayer on Cu(001) is a strong ferromagnet in the whole concentration range.[12] The effective pairwise interchange interactions support this picture, since they are in turn 1.97, −0.63, 0.22, 0.09, −0.31, 0.05, −0.05, 0.00, −0.08, 0.11, 0.00 mRy for the first 11 neighbor shells for the $\mathrm{Fe}_{50}\mathrm{Co}_{50}$ bulk alloy. For a $\mathrm{Fe}_{50}\mathrm{Co}_{50}$ overlayer on Cu(001) we obtain 2.86, 0.21, −0.56, 0.20, −0.05, 0.19, 0.02, 0.02, 0.00 −0.01, 0.00 mRy. The following pair and all triplet interactions are of the order of 0.05 mRy or less.

Clearly, nearest-neighbor interactions dominate in both cases. The dominating positive first nearest-neighbor interchange interaction implies a strong ordering tendency for both the bulk and the overlayer alloys. Note, however, that the pairwise interactions just indicate a tendency towards ordering, but are, by themselves, not sufficient to determine which superstructure is formed. For the paramagnetic case, the corresponding values for the nearest-neighbor interaction are −0.7 and −1.96 mRy for the bulk and the overlayer alloys, respectively.

The evaluation of the compositional ordering temperature T^{ord} is quite a delicate problem. As already mentioned, the effective-medium estimate of T^{ord} [see Eq. (3)] can be improved by using Monte Carlo simulations which show, however, a clear dependency on the number of shells included.

There is no reason that the mean-field (MF) and Monte Carlo (MC) results coincide even by taking into account interactions beyond the first and second nearest-neighbor interactions. As a demonstration, a study of the critical temperature of the order-disorder transition in the bulk 50-50 alloy is shown. The MC simulations have been performed in the grand canonic ensemble, using a total of 11 664 sites and three-dimensional periodic boundary conditions. For each temperature, the properties of the equilibrium state, as defined by the long-range-order (LRO) parameter, is obtained by performing 5000 MC steps/site. As the order-disorder transition is continuous (second order), the critical temperature is obtained by plotting the square of the LRO parameter versus temperature. Sufficiently close to the transition, $(\mathrm{LRO})^2$ varies linearly and its extrapolation to the T axis defines the critical temperature T^{ord}. Figure 2 shows the T^{ord} val-

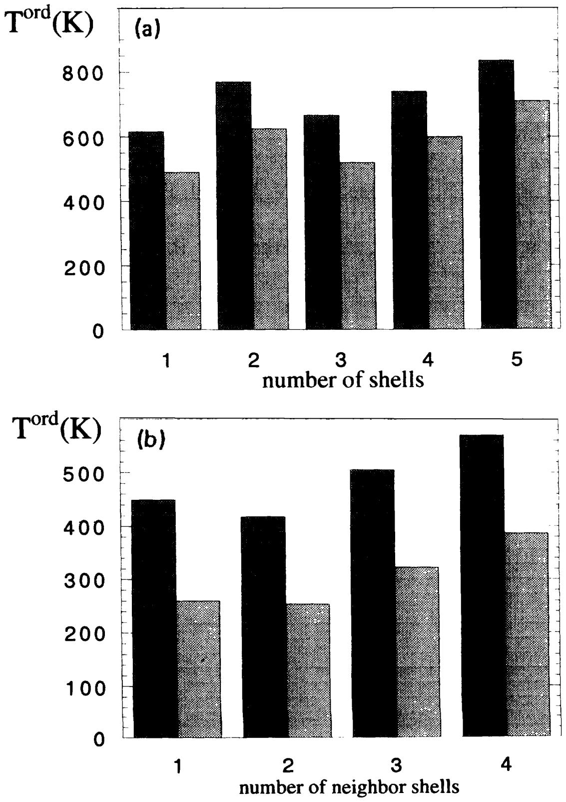

FIG. 2. Values of T^{ord} as a function of the nearest-neighbor shells of pairwise interactions included: (a) bulk and (b) overlayer. The mean-field and Monte Carlo results are shown as dark and light grey stacks, respectively.

ues as a function of the number of nearest-neighbor shells of pair interactions included in statistical simulations for both the MF and the MC methods. Restriction up to the fifth nearest neighbors gives a MF critical temperature which corresponds to 90% of the MF critical temperature obtained with a total of up to 11th nearest neighbors. Using therefore the first five interactions seems to be a good approximation for the calculation of $T^{\rm ord}$. This is not the case considering only the first and the second nearest interactions as is shown in Fig. 2. Compared to the MC simulations, the MF results overestimate $T^{\rm ord}$ by about 20% in each case. One can also see that $T^{\rm ord}$ does not vary linearly with the number of shells included. Using 11 interactions, the effective-medium estimate of $T^{\rm ord}$ yields 917 K as compared with the experimental value of 1006 K. For the overlayer case, the difference between the MF and the MC results is more dramatic since the validity of the effective medium is less justified due to the reduced translational symmetry. In Fig. 2(b) the MC and the MF $T^{\rm ord}$ values are shown as a function of the number of shells included. The conclusions to be drawn for the surface case are quite similar to the bulk case. For a given set of interactions the MF results overestimate $T^{\rm ord}$ by about 40%. The dependency of $T^{\rm ord}$ on the number of shells is not linear. There is no experimental data for the order-disorder transition temperature for a $\mathrm{Fe}_{50}\mathrm{Co}_{50}$ overlayer on a Cu(001) substrate. A comparison to the bulk values shows a strong decrease of $T^{\rm ord}$, which essentially is due to the difference in the coordination numbers, since the first nearest-neighbor effective pair interaction is by 40% higher in the overlayer case.

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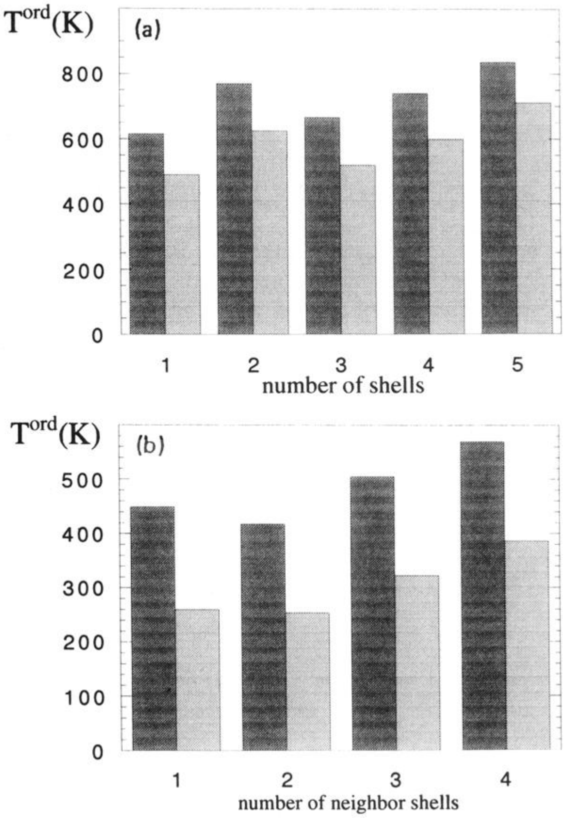

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