

Theory for the effects of the local atomic environment on the formation of magnetic moments*

K. Aoi, H. Deuling, and K. H. Bennemann

Institute for Theoretical Physics, Freie Universität Berlin, 1 Berlin 33, Germany

(Received 4 March 1974)

The effect of the local atomic environment on the formation of magnetic moments is studied by a model calculation using an extension of the coherent-potential approximation which includes local-atomic-environment effects. The calculation shows that, depending on the d -electron number, the local atomic environment may both enhance as well as decrease the magnetic moment of an atom.

Recently, many experiments have studied the effect of the local atomic environment on the formation of local magnetic moments.¹⁻³ In many cases the interesting dependence of the magnetic moments on the surrounding atomic environment occurs in concentrated alloys. It is observed that the local atomic environment may enhance as well as decrease the local magnetic moment.⁴ For example, in the case of Ni in CuNi alloys the Ni atoms help each other to obtain a magnetic moment while in the case of V in disordered Au₄V the V atoms help each other to quench their local magnetic moment they possess in ordered Au₄V.

There exist only a few theoretical studies⁵⁻⁸ of the dependence of the local magnetic moments on the interaction among the magnetically active impurities. However, these theories are limited to dilute alloys. Since local environment effects frequently appear most dramatically in concentrated alloys, alloy theory valid for concentrated alloys needs to be used.⁹ Recently, Brouers *et al.*¹⁰ and Aoi¹¹ have extended the single-site coherent-potential approximation (CPA) in order to include local-atomic-environment effects.

In the following we shall study the effect of the atomic environment on the formation of local magnetic moments by further extending the theory by Aoi¹¹ to include the effect of Coulomb interactions between d electrons with different spins. Thus, the present work presents an extension to concentrated alloys of the papers by Alexander and Anderson⁵ and others⁶⁻⁸ on the impurity-impurity coupling. We use for the d electrons the Hamiltonian

$$H = \sum_{i \neq j} h_{ij} C_{i\sigma}^\dagger C_{j\sigma} + \sum_{i,\sigma} (\epsilon_i^0 + U_i C_{i-\sigma}^\dagger C_{i-\sigma}) C_{i\sigma}^\dagger C_{i\sigma}, \quad (1)$$

where C_i^\dagger and C_i are the usual creation and annihilation operators for d electrons with spin σ at the site i , and h_{ij} denotes the hopping matrix element between the atomic sites i and j . We assume that

h_{ij} is independent of the type of atoms at the sites i and j . The d -electron energy ϵ_i^0 takes either of the values ϵ_A^0 or ϵ_B^0 depending on whether an atom of type A or B occupies the site i . U_i is the Coulomb interaction potential between electrons with different spins at site i . The local Green's function for a d electron at site i with spin σ is then given by

$$G_{ii,\sigma} = G_{ii} + \sum_{j,k} G_{ij} T_{jk,\sigma} G_{ki}, \quad (2)$$

where G_{ij} is the CPA Green's function,⁹ and the T matrix has the form

$$T_{jk,\sigma} = t_{j\sigma} \delta_{jk} + (1 - \delta_{jk}) t_{j\sigma} G_{jk} t_{k\sigma} + \sum_{l \neq j} t_{j\sigma} G_{jl} t_{l\sigma} G_{lk} t_{k\sigma} + \dots \quad (3)$$

Here, the spin-dependent t -matrix $t_{j\sigma}$ is given by

$$t_{j\sigma} = (\epsilon_{j\sigma} - \Sigma) / [1 - (\epsilon_{j\sigma} - \Sigma) G_{jj\sigma}], \quad (4)$$

where Σ denotes the CPA self-energy. Within Hartree-Fock approximation one has

$$\epsilon_{j\sigma} = \epsilon_j^0 + U_j \langle n_{-\sigma} \rangle \quad (5)$$

and (for low temperatures)

$$\langle n_{j\sigma} \rangle = -\frac{1}{\pi} \int_{-\infty}^{\epsilon_F} d\epsilon \operatorname{Im} G_{jj,\sigma}(\epsilon). \quad (6)$$

Clearly, the number of d electrons with spin i at site i , $\langle n_{i\sigma} \rangle$, and therefore $\epsilon_{i\sigma}$ depend on the local atomic environment as well as on the species of atom at site j . The local magnetic moment at site i is given by

$$m_i = \mu_B (\langle n_{i\uparrow} \rangle - \langle n_{i\downarrow} \rangle). \quad (7)$$

We determine now $\langle n_{i\sigma} \rangle$. For this T_{jk} is calculated by breaking up all the scattering paths at various atomic sites into elementary paths.¹¹ In the following we shall specify the local atomic environment around the site i by giving the number n_A and n_B of A and B atoms in the first atomic shell around i and by assuming that sites beyond the first shell are treated by the CPA medium. Then,

taking into account only the most important scattering processes involving the first shell, which are shown in Fig. 1, we obtain

$$G_{ii,\sigma} = G_{ii} + \frac{G_{ii}^2 t_{i\sigma} + 2G_{ii} G_{i1}^2 y_{\sigma} t_{i\sigma} + G_{i1}^2 y_{\sigma}}{1 - G_{i1}^2 t_{i\sigma} y_{\sigma}}, \quad (8)$$

where $G_1 \equiv G_{ij}$ with i and j referring to nearest-neighbor sites and where

$$y_{\sigma} = n_A t_{A\sigma} + n_B t_{B\sigma}. \quad (9)$$

Furthermore, in the following we assume that atoms in the first shell are surrounded by the CPA medium, and therefore drop the spin dependence σ of y . Then given the quantity $\delta \equiv (\epsilon_A - \epsilon_B)/W$, one can determine t_j for sites j in the first shell by carrying out the conventional CPA calculation. Here, W is the half-bandwidth and

$$\epsilon_L = \epsilon_L^0 + U_L \langle\langle n_L \rangle\rangle, \quad L = A, B \quad (10)$$

with $\langle\langle n_L \rangle\rangle$ denoting the expectation value of the electronic occupation number of the atom of type L which is surrounded by the CPA medium.

Since the numerical calculation of G_1 for a realistic model density of states is complicated, we shall calculate G_1 for the case of the simple cubic lattice and the corresponding tight-binding-model density of states.

Shown in Fig. 2 is the local density of states of a nonmagnetic atom for various configurations and for $\delta = 0.45$ and $C_A = 0.2$. This calculation is not fully self-consistent since $\epsilon_{A\sigma}$ is approximated by ϵ_A as given by Eq. (10).¹² It should be pointed out that for the atomic configuration A(0A) there is only one peak in the local density of states, while for A(6A), A(5A), and A(4A) the peak splits into two. Here, A(6A) denotes an atomic configuration where the atom A is surrounded by six nearest-neighbor A atoms. The above splitting in $\rho(\epsilon)$ is

$$T_{ii}^{(\sigma)} = \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} + \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} + \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} + \dots$$

$$T_{ji}^{(\sigma)} = \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array}; \quad T_{ik}^{(\sigma)} = \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array}$$

$$T_{ji}^{(\sigma)} = \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} + \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array}$$

FIG. 1. Electronic scattering processes contributing to the local density of states and involving the local atomic environment. The central site under consideration is i and j, k, l, \dots are nearest-neighbor sites of i . The open circles represent the t matrices at indicated sites, and the solid lines with arrows are the CPA Green's function.

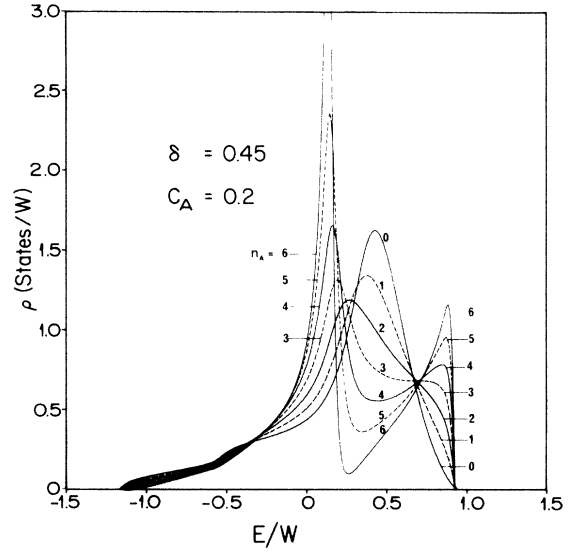


FIG. 2. Local density of states for sites occupied by nonmagnetic A atoms with n_A A atoms in the nearest-neighbor sites.

the covalent splitting which is caused by hybridization of the energy level of the A atom at the central site with those of the nearest neighbors. In order to demonstrate this more clearly, let us consider the case where all of the nearest-neighbor sites are occupied by A atoms. The energy levels, in the presence of hybridization h between the central atom and each of the nearest-neighbor atoms, can be obtained by diagonalizing the $(N+1) \times (N+1)$ matrix:

$$\begin{pmatrix} \epsilon_A & h & h & \dots & h \\ h & \epsilon_A & 0 & \dots & 0 \\ h & 0 & \epsilon_A & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ h & 0 & 0 & \dots & \epsilon_A \end{pmatrix}.$$

The resulting eigenvalues are ϵ_A [($N-1$) degenerate] and $\epsilon_A \pm N^{1/2}h$. Furthermore one can show that the eigenstates which correspond to the ($N-1$) degenerate levels do not refer to the Wannier state at the central site. Thus the energy spectrum at the central site consists of two δ functions at $\epsilon_A \pm N^{1/2}V$. In the present case these two levels mix with the CPA medium, giving rise to two broadened levels in the local density of states. As a consequence of this splitting the local density of states for $A(n_A A)$ at $\epsilon/W \sim 0.5$ increases with decreasing values of n_A . Therefore, if the Fermi energy ϵ_F is at $\sim 0.5W$, the A atom acquires more easily a local magnetic moment when it does not have A atoms on its nearest-neighbor sites. On the other hand if $\epsilon_F/W \sim 0.8$, A atoms which have more A

atoms in the nearest-neighbor sites are more likely to be magnetic. The former case might be the situation for Au_4V , while the latter case might be the situation for CuNi alloys. There are more holes in the electron band in $\text{Au}_{0.8}\text{V}_{0.2}$ than in $\text{Cu}_{0.8}\text{Ni}_{0.2}$. Thus, ϵ_F is lower for Au_4V than for CuNi relative to their band edges.

The result of a self-consistent calculation for $U_A = 0.65W$, $U_B = 0$, and $\epsilon_F = 0.4W$ is shown in Fig. 3. This simulates presumably the situation for Au_4V . Plotted in Fig. 3 is the density of states for both spin directions for the atomic configuration $A(0A)$. For these values no magnetic moments appear for other atomic configurations than $A(0A)$.

In Table I we summarize the results for the dependence of the magnetic moments on the atomic environments for $U_B = 0$ and various values of U_A and ϵ_F/W . The cases with $\epsilon_F/W = 0.75$ should simulate the situation in $\text{Cu}_{0.8}\text{Ni}_{0.2}$. For $U = 2.8W$, local magnetic moments appear for configurations $A(6A)$ and $A(5A)$, and no moments appear for other configurations. This value of U_A is larger than the accepted value for nickel, but for smaller values of U_A we do not obtain moments. This discrepancy is due to the fact that we have used an oversimplified model density of states rather than a realistic band corresponding to Cu or Ni. It is well known that in $3d$ bands, there is a sharp peak near the upper band edge. Furthermore, the coordination number for the face-centered-cubic lattice is 12 as compared to 6 for the simple cubic lattice. Both of these facts help real systems to form for smaller values of U_A larger local magnetic mo-

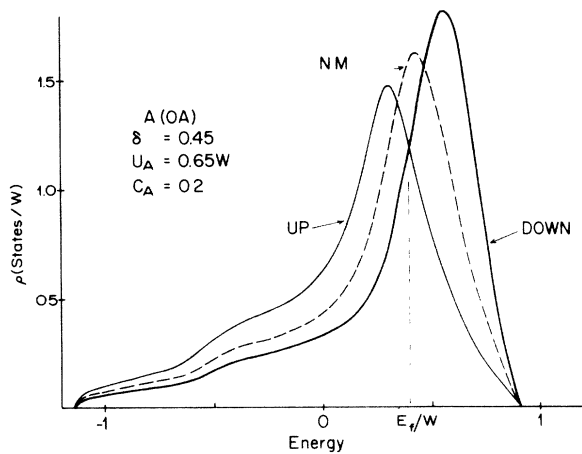


FIG. 3. Self-consistent local density of states for up and down spin directions for the atomic configuration $A(0A)$. The dashed curve refers to the nonmagnetic A atoms.

TABLE I. Local magnetic moments m_A in unit of the Bohr magneton for an atom A which is surrounded by n_A nearest-neighbor A atoms. The Fermi level is assumed to be $0.4W$ and $0.75W$. The former is to simulate $\text{Au}_{0.8}\text{V}_{0.2}$ and the latter, $\text{Cu}_{0.8}\text{Ni}_{0.2}$. m_A is calculated for $\delta = 0.45$, $C_A = 0.2$, and $U_B = 0$ and for various values of U_A . Note that the appearance of local magnetic moments is in accordance with the criteria $[-U_A(\partial\langle n_{i\sigma} \rangle / \partial \epsilon_{i\sigma})] > 1$.

n_A	$\epsilon_F/W = 0.4$			$\epsilon_F/W = 0.75$	
	$U_A/W = 0.6$	0.65	0.70	2.7	2.8
0	0.14	0.35	0.45	0	0
1	0	0	0.21	0	0
2	0	0	0	0	0
3	0	0	0	0	0
4	0	0	0	0	0
5	0	0	0	0	0.08
6	0	0	0	0.09	0.13

ments for particular atomic configurations. Nevertheless, our model calculations show clearly essential aspects of the formation of the local moment.

The present theory for the local-atomic-environment effects is similar to previous theories.¹⁰ However, in contrast to Brouers, Cyrot, and Cyrot-Lackman¹⁰ we find no peak in the local density of states for the $A(6A)$ configuration at the energy where $A(0A)$ has a peak. As already discussed above we believe that because of the covalent splitting there should be a dip, rather than a peak, at this energy.

Note that our theory¹¹ can include local-environment effects due to scattering processes of the type $t_i G_{il} t_l G_{lm} t_m$, where l and m are nearest neighbors of i . In the above numerical calculation, however, we have not included such terms. This is because we have used a simple cubic lattice and for this lattice structure the above scattering processes include at least one Green's function involving next-nearest-neighbor hopping. Since we are assuming a tight-binding band and are specifying only the nearest-neighbor atoms while neglecting entirely the next-nearest-neighbor hopping, such terms need not be considered here.

In conclusion, we find that the local atomic environment plays an important role for the appearance of the local magnetic moment when the average medium is almost magnetic, and that a certain local environment can enhance as well as decrease the local moment depending on the position of the Fermi level.

We wish to thank Professor K. D. Schotte, U. Forwergck and Professor J. Garland for useful discussions.

*Research supported partly by DFG under Grant No. SFB 161.

¹C. G. Robbins, H. Claus, and P. Beck, Phys. Rev. Lett. 22, 1307 (1969); H. Claus, A. K. Sinha, and P. Beck, Phys. Lett. A 26, 38 (1967).

²T. J. Hicks, B. Rainford, J. S. Kouvel, G. G. Low, and J. B. Comly, Phys. Rev. Lett. 22, 531 (1969).

³L. Creveling, H. Luo, and G. S. Knapp, Phys. Rev. Lett. 18, 851 (1967).

⁴P. Beck, Metall. Trans. 2, 2015 (1971).

⁵S. Alexander and P. W. Anderson, Phys. Rev. 133, 1595 (1964).

⁶S. Liu, Phys. Rev. 163, 472 (1967).

⁷T. Moriya, Progr. Theoret. Phys. 33, 157 (1965).

⁸D. J. Kim, Phys. Rev. B 1, 3725 (1970); K. H. Bennemann and J. W. Garland, J. Phys. 32, C1-750 (1971).

⁹P. Soven, Phys. Rev. 178, 1136 (1969).

¹⁰F. Brouers, M. Cyrot, and F. Cyrot-Lackman, Phys. Rev. B 7, 4370 (1973); F. Brouers, F. Ducastelle, F. Gautier, and J. Van Der Rest, J. Phys. F 3, 2120 (1973).

¹¹K. Aoi, Solid State Commun. (to be published).

¹²For a fully self-consistent calculation it is necessary to specify ϵ_F , because otherwise $\langle n_{i-\sigma} \rangle$ cannot be determined. However, the fully self-consistent density of state is very similar to those shown in Fig. 2 for the same values of δ and C_A .