

First-principles KKR-CPA calculation of interactions between concentration fluctuations

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 365232

(<http://iopscience.iop.org/0953-8984/19/36/365232>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 04:38

Please note that [terms and conditions apply](#).

First-principles KKR-CPA calculation of interactions between concentration fluctuations

N H Long and H Akai

Department of Physics, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka 560-0043, Japan

E-mail: longnh@presto.phys.sci.osaka-u.ac.jp

Received 19 December 2006, in final form 21 March 2007

Published 24 August 2007

Online at stacks.iop.org/JPhysCM/19/365232

Abstract

The aim of this work is to develop the method of calculating atomic interactions in metals and semiconductors on the basis of first-principles electronic structure calculation. A new method to calculate the atomic interactions in the framework of KKR-CPA is proposed. In this approach two specific atoms embedded in a CPA medium are considered and the effects of both electron–electron interactions and multiple scattering, which are neglected in the generalized perturbation method (GPM), are fully taken into account. The calculated atomic interactions show that these effects are important for alloys containing transition-metal alloys such as FeAl. On the other hand, in the case of AuCu, where the d states lie considerably below the Fermi level, the effects are less important.

1. Introduction

Chemical ordering, including short-range ordering and long-range ordering, is observed in many substitutional alloys. The ordering emerges in disordered states as a result of atomic interactions acting between atoms in the disordered state. Strong or weak interactions, as well as the sign of these interactions, determine the chemical ordering. They also determine various physical properties such as cohesive, structural and magnetic properties. The atomic interactions in alloys have long been studied theoretically. Some of them are based on perturbation theory. Others rely more or less on interpolation or extrapolation schemes. None of those, however, are powerful enough to predict the precise phase diagram of experimentally unknown systems or the subtle self-organizing structure of doped systems, and so on. To develop methods that enable us to accurately calculate the ordering energy of disordered alloys and doped systems in a systematic way is thus one of the challenges for many researchers in this field.

A starting point of the study is to expand the configuration energy into cluster interactions of Ising-like form, where the occupation number of a particular atom at each site is used

in place of magnetic moments. These are often called effective cluster interactions, ECIs. Along this line, many authors have developed methods to calculate the ordering energy of disordered systems. One of the methods is the Connolly–William method (CWM) [1]. In this method, Connolly and William derived a cluster expansion from a series of density-functional calculations on various ordered compounds. They gave a definition of the correlation function ξ corresponding to each type of structure, and expressed the configuration energy as a sum of many-body interaction potentials $v_n(r)$ weighted by the correlation functions. This method has been widely applied for constructing the phase diagram of binary alloys [2, 3] and oxides [4]. However, the convergence of the expansion is not necessarily fast, which is a main drawback of this method. Alternatively, one may use generalized perturbation method (GPM) type schemes. Such schemes are less problematic concerning the convergence.

The GPM theory was first proposed by Ducastelle and Gautier [5, 6] in 1976. In their work, the determination of a configuration energy was performed in terms of effective cluster interactions within the framework of the embedded cluster method (ECM) that was based on the idea of Kikuchi (the cluster variation method—CVM [7]). The basis of this method is the use of completely disordered states, which are described in the coherent potential approximation (CPA), as an appropriate reference medium. Later, Gonis *et al* [8] gave a clear definition of effective pair interactions by evaluating the atomic interactions. In intensive studies, Turchi *et al* [9] employed the GPM combined with the Korringa–Kohn–Rostoker (KKR) method and local density approximation (LDA) of the density functional method to calculate the effective pair interactions for substitutional alloys PdV and PdRh. The ordering and segregating tendencies of these alloys, which were obtained by the theoretical calculation, are in reasonable agreement with experimental results. However, in their approach, due to the perturbative nature of the GPM, only the second-order scatterings could be taken into account to determine the effective pair interactions. Moreover, they neglected the effects of the electron–electron interaction on the atomic interactions, which could be important in correlated systems.

The purpose of the present study is to determine the atomic interactions more accurately by taking account of both multiple scattering and electron–electron interaction effects. In this approach, by embedding two impurities in a CPA medium, the atomic interaction energy can be calculated self-consistently. We use the present method to calculate the effective pair interactions of several binary alloys to see the applicability of the method. The results show that the effects of electron–electron interactions and multiple scattering are significant in the case of transition-metal alloys such as FeAl. In contrast, in AuCu, where the d states lie considerably below the Fermi level, these effects are less important.

2. Theoretical framework

2.1. Generalized perturbation method in KKR-CPA

Based on the calculation using the first-principles KKR method, a completely disordered state can be determined in the CPA. Starting from this completely disordered state, the configuration energy is expanded into the concentration fluctuation δc . The second-order effective cluster interaction in this scheme, which is obtained from the k th-order effective cluster interaction defined in [9] by putting $k = 2$, is

$$V_{ij} = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{\epsilon_F} d\epsilon \text{Tr} [\Delta(\epsilon) \tau_{ij}(\epsilon) \Delta(\epsilon) \tau_{ji}(\epsilon)] \quad (1)$$

with $\Delta(\epsilon) = t_A^{-1}(\epsilon) - t_B^{-1}(\epsilon)$ and

$$\tau_{ij}(\epsilon) = \sum_{\vec{k}} \left[t^{-1}(\epsilon) - g(\vec{k}, \epsilon) \right]^{-1} \exp \left[i\vec{k}(\vec{R}_i - \vec{R}_j) \right]. \quad (2)$$

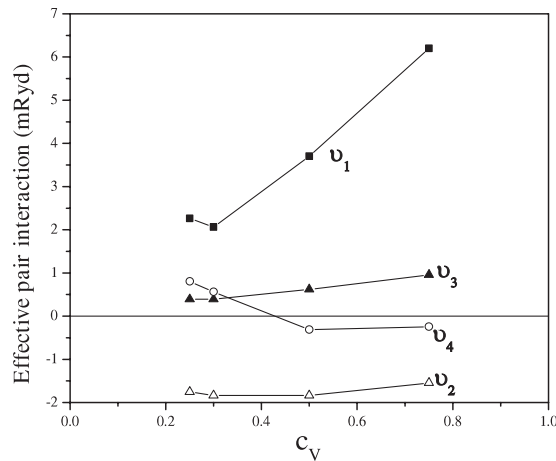


Figure 1. Effective pair interactions up to fourth-neighbour shell as functions of the vanadium concentration for PdV substitutional alloys.

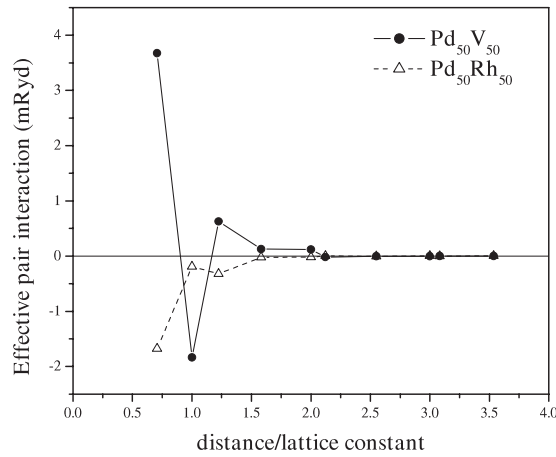


Figure 2. Effective pair interactions as functions of the distance between the atoms for $Pd_{1-c}V_c$ and $Pd_{1-c}Rh_c$ alloys at $c = 0.5$.

Here, $t_{A(B)}^{-1}$ is the inverse t -matrix of the A(B) atom, t is the coherent t -matrix, and \vec{R}_i denotes the position of the i th impurity atom. It is clear that only the second-order scattering is taken into account in these equations. Also, the effects of the electron–electron interaction, which could be partly included if a self-consistent procedure we will propose were used, are completely neglected.

To illustrate the above method, we calculated the case of PdV and PdRh substitutional alloys, which were also calculated by Turchi *et al*, on an underlying fcc structure. The results are shown in figures 1 and 2. Our calculation for the effective pair interaction (second-order term) up to the fourth-nearest neighbours of the PdV system at some different concentrations of vanadium is essentially the same as those given by Turchi *et al* [9]. The tendency towards ordering of PdV and that towards phase separation of PdRh systems, corresponding to positive or negative effective pair interactions, shown in figure 2, are in reasonable agreements with

experimental ones. The calculations here were performed by GPM code that was implemented in the MACHIKANNEYAMA KKR-CPA-LDA code [10].

2.2. Inclusion of multiple scattering

In order to improve the GPM theory, we propose a method which calculates the atomic interactions of the substitutional system including the effects of multiple scattering and electron–electron interaction. The basic idea of the approach is that the effective pair interaction can be directly calculated by embedding two impurities in the host CPA medium. By calculating the scattering path operator as well as the Green’s function where the two specific atoms are embedded in the CPA medium, we compare the energy of systems for three different cases: A–A, A–B and B–B pairs embedded in a completely disordered binary AB system. The effective pair interaction is now obtained as the differences in energy between these cases:

$$V_{ij} = \Delta E_{AA} + \Delta E_{BB} - 2\Delta E_{AB}. \quad (3)$$

The electronic structure of two embedded impurities, for which multiple scattering between two impurities occurs, is solved using the scattering path operator matrix containing two blocks corresponding to the two impurity atoms:

$$\tau = \begin{pmatrix} \tau_{ii} & \tau_{ij} \\ \tau_{ji} & \tau_{jj} \end{pmatrix}. \quad (4)$$

Thus obtained τ is used to calculate the corresponding quantity B [11] for the scattering of the impurity pair system:

$$B = \begin{pmatrix} t_i^{-1} - t^{-1} - (\tau^{-1})_{ii} & -(\tau^{-1})_{ij} \\ -(\tau^{-1})_{ji} & t_j^{-1} - t^{-1} - (\tau^{-1})_{jj} \end{pmatrix}^{-1}. \quad (5)$$

From B , the back-scattering part of the Green’s function is obtained and the charge density is constructed from it. The change in the band energy ΔE_{band} due to embedding an impurity pair in the system is also calculated directly from B . The effective pair interaction including multiple scattering is now obtained from equation (3) by comparing the changes in the band energy of the embedded case from the non-embedded case, $\Delta E_{\text{band}}^{\text{AA}}$, $\Delta E_{\text{band}}^{\text{BB}}$ and $\Delta E_{\text{band}}^{\text{AB}}$.

In figure 3, the effective pair interactions of the PdV system for various concentrations of vanadium, calculated from the differences in the band energy including the multiple scattering effects described above, are compared with the GPM results calculated according to Turchi’s approach. The values of effective pair interaction are essentially unchanged from that obtained by Turchi’s approach. Hence, it is concluded that the effect of multiple scattering is not significant in these cases.

2.3. Self-consistent determination of atomic interactions

To further improve the calculation, we introduce the effects of electron–electron interaction on the atomic interaction. The change in the electron–electron interaction depends on the specific type of atom pairs and is obtained from the total energy of the system calculated self-consistently with two impurity pairs embedded in the CPA medium. The total energy of the system can be expressed as

$$E^{\text{tot}} = T + E^{\text{stat}} + E^{\text{xc}}. \quad (6)$$

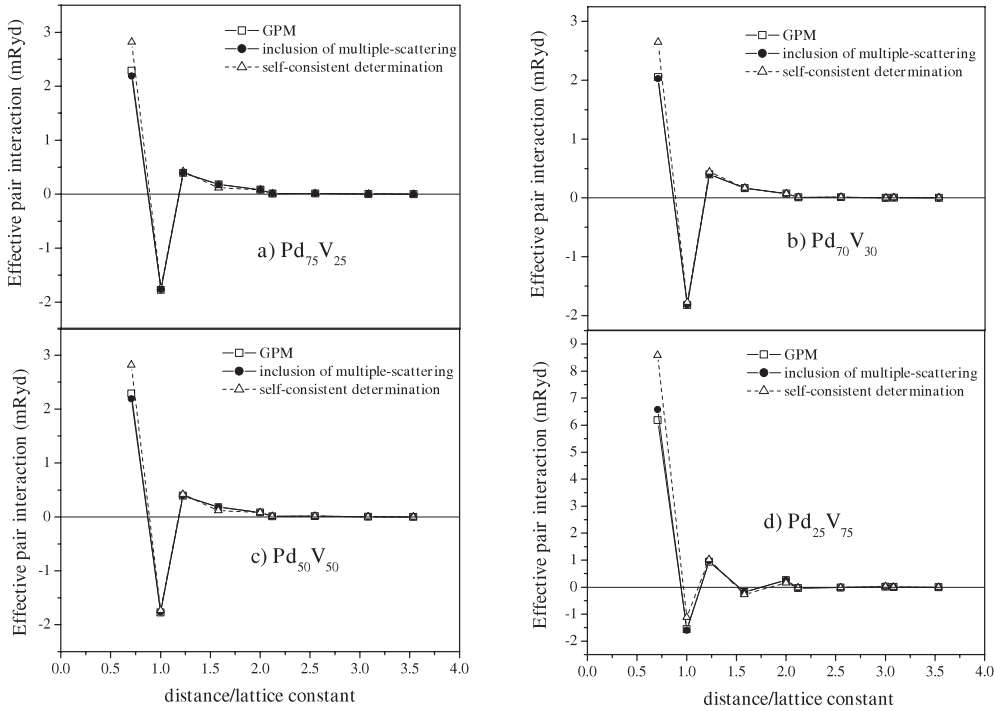


Figure 3. Effective pair interactions as functions of the distance between the atoms for $\text{Pd}_{1-c}\text{V}_c$, at $c = 0.25$ (a), $c = 0.3$ (b), $c = 0.5$ (c) and $c = 0.75$ (d).

The kinetic energy T of non-interacting system in the sense of the local density functional theory is calculated by subtracting the potential energy $E^{\text{pot}} = \sum_{\sigma} \sum_{i=A,B} c_i \int_0^{R_{\text{MT}}} dr r^2 \rho_{\sigma}^i(r) v_{\sigma}^i(r)$ from the band energy that is obtained in section 2.2. Here i indicates the species of the component atoms and c_i is the concentration of the i th species; ρ_{σ}^i and v_{σ}^i are respectively the charge density and the effective potential of each component atom. The exchange–correlation energy E^{xc} is calculated within the LDA. The electrostatic energy E^{stat} includes both electron–electron (Hartree energy) and electron–nucleus (external potential) contributions. This term needs special care since usual KKR–CPA–LDA does not take account of the effect of the charge redistribution on the long-range electrostatic interaction that may occur by placing a specific impurity atom in the medium. We calculate E^{stat} in the following way. In the usual procedure, the electrostatic energy is calculated from self-consistent charges associated with an impurity embedded in a totally charge neutral CPA medium. The final expression in general is summarized as

$$E^{\text{stat}} = QV + E^{\text{stat inside}}, \quad (7)$$

where $Q = \sum_{i=A,B} c_i Q_i$ is the average total charge inside the muffin-tin sphere at site i and V is the electrostatic potential of the medium associated with each site:

$$V = AQ. \quad (8)$$

Here, A is the Madlung coefficient, which depends on the crystal structure. $E^{\text{stat inside}}$ is the electrostatic energy due to the charges inside the muffin-tin sphere, which can be calculated locally for each site. Using the Madlung-type potential V , the electrostatic energy caused by an impurity pair embedded in the CPA medium can be treated in the following way: suppose

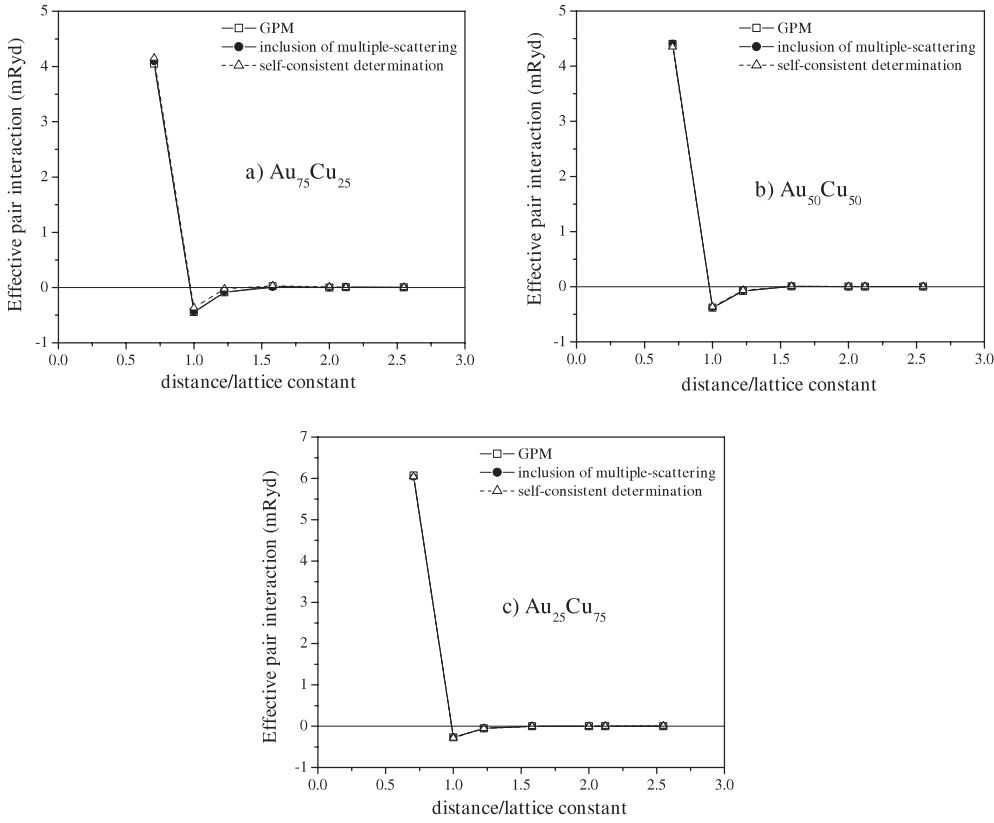


Figure 4. Effective pair interactions as functions of the distance between the atoms for $\text{Au}_{1-c}\text{Cu}_c$, at $c = 0.25$ (a), $c = 0.5$ (b) and $c = 0.75$ (c).

that impurities A (charge Q_A) and B (charge Q_B) are located at site i and j , respectively. First we notice that the change in $Q_{A(B)}$ is rather small even for an impurity pair formed by nearest neighbours, typically $10^{-3} \sim 10^{-5}$ in metallic systems. In such cases, the change in the interatomic electrostatic energy to the first order in $\Delta Q_{A(B)}$, which is the change in $Q_{A(B)}$ due to the existence of the second impurity at the near neighbour, would be enough for the calculation of the atomic interactions. Then the change in the electrostatic energy ΔE^{stat} is well approximated as

$$\Delta E^{\text{stat}} = (\Delta Q_A + \Delta Q_B)V + \Delta E^{\text{stat inside}}. \quad (9)$$

After the self-consistency is attained, the total energy is compared with that of disordered state described by the CPA medium. Then, the effective pair interaction can be directly obtained by use of equation (3).

Figure 3 shows the effective pair interactions of binary PdV alloy obtained by the above self-consistent procedure. It is seen that the differences in the effective pair interactions between the self-consistent determination and the GPM are considerable for first four nearest distances. Therefore, we can conclude that the effect of the electron–electron interactions cannot be neglected for a reliable description of the effective pair interaction. Furthermore, in the present scheme the pair interactions show a rapid convergence with increasing distance between the atoms, which is known as an advantage of the GPM.

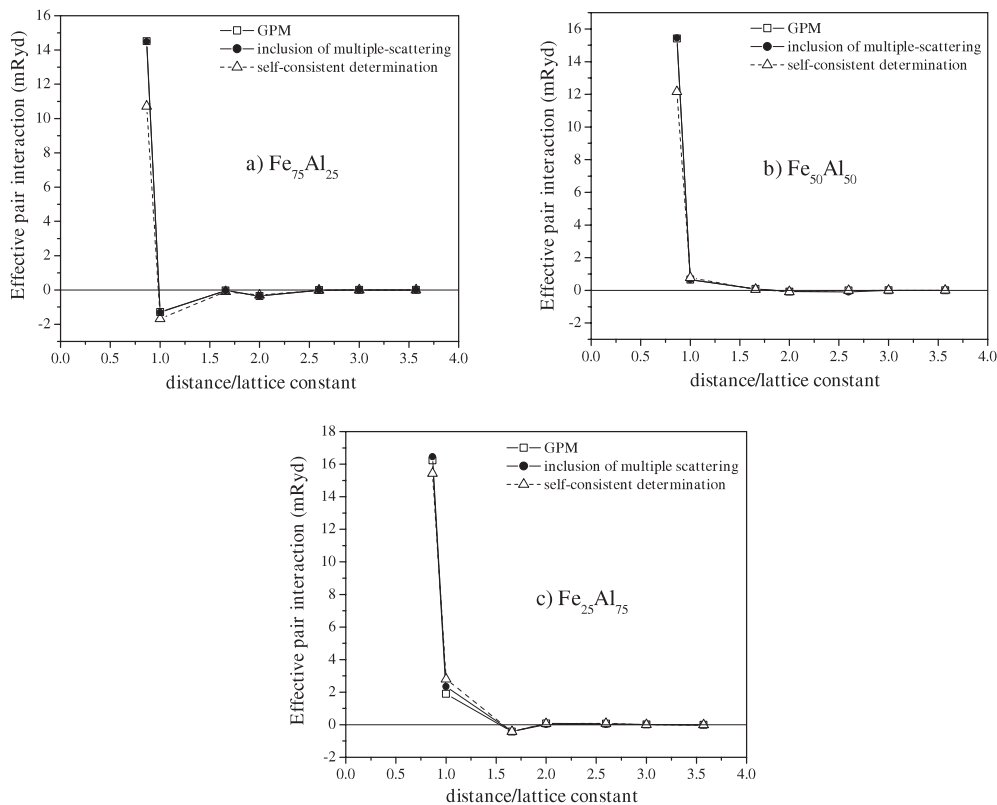


Figure 5. Effective pair interactions as functions of the distance between the atoms for Fe_{1-c}Al_c, at $c = 0.25$ (a), $c = 0.5$ (b) and $c = 0.75$ (c).

3. Effective pair interaction for AuCu and FeAl systems

In this section, the applications of our new method to AuCu and FeAl binary alloy systems are presented. In the AuCu system, the relativistic effects, except the spin-orbit interaction, are included in order to make the comparison with other calculations possible [12], though the FeAl system is treated in a non-relativistic scheme. For all cases, the lattice constants of systems at the completely disordered state are determined from the minimum of the total energy as a function of the lattice constant.

Figure 4 shows the effective pair interactions of AuCu alloys as functions of the distance between the atoms. Each plot corresponds to the concentration of Cu being 0.25, 0.5 and 0.75, respectively. It might be expected that the effect of the electron-electron interaction would be rather strong for both transition and noble metals. In the case of AuCu, however, there are no remarkable differences in the effective pair interactions calculated by the GPM and the present method. This may indicate that the electron-electron interaction is well screened by *s* and *p* electrons in the cases where the *d* states lie rather deep below the Fermi energy.

The effective pair interactions obtained by the differences in the band energy, i.e., inclusion of the two-atom multiple scattering, also are rather unchanged from the results of the GPM calculation (see figure 4 for the AuCu system and figure 5 for the FeAl system). In these cases, it is also concluded that neglecting the multiple scattering might not be a critical drawback.

To see the effect of electron–electron interaction on the atomic interaction in the case of transition-metal alloys, we investigate the effective pair interactions for FeAl. In this system, in contrast to AuCu, the values of effective pair interactions change considerably, as shown in figure 5. Figures 5(a)–(c) correspond to the cases of the concentration of Fe is 0.75, 0.5 and 0.25, respectively. In figures 5(a) and (b), for which the concentration of Fe is rather high, we can see that the differences in the effective pair interactions between the GPM and the self-consistent determination are remarkable. On the other hand, in the case shown in figure 5(c), where the concentration of Fe is low and the screening due to s and p states is more effective, the difference is relatively small. From these observations, in the case of FeAl, we conclude that the effects of the electron interaction are considerable and cannot be neglected.

4. Conclusion

We have developed a new approach to calculate pair interactions of alloy systems. This approach deals with two embedded atoms in the CPA medium in the framework of the first-principles KKR-CPA method. The effects of multiple scattering and electron–electron interaction, which are completely neglected in the GPM, are taken into account in this approach. From the calculation for PdV and FeAl systems, it is concluded that the effect of the electron–electron interaction is rather important in determining the effective atomic pair interaction. On the other hand, in the case of the AuCu system, where the main d states lie below the Fermi level, the treatment neglecting both the electrons interaction and multiple scattering seems still to work. An investigation using the present method for doped semiconductor systems, for which the effects of multiple scattering are known to be important, is now going on.

References

- [1] Connolly J W and Williams A R 1983 *Phys. Rev. B* **27** 5169
- [2] Mohri T, Terakura K, Takizawa S and Sanchez J M 1991 *Acta Metall. Mater.* **39** 493
- [3] Hoshino T, Schweika W, Zeller R and Dederichs P H 1993 *Phys. Rev. B* **47** 5106
- [4] A F Kohan 1997 *Doctor Thesis* Massachusetts Institute of Technology
- [5] Ducastelle F and Gautier F 1976 *J. Phys. F: Met. Phys.* **6** 2039
- [6] Ducastelle F 1991 *Order and Phase Stability in Alloys* (Amsterdam: North-Holland)
- [7] Kikuchi R 1951 *Phys. Rev.* **81** 988
- [8] Gonis A, Zhang X G, Freeman A J, Turchi P, Stocks G M and Nicholson D M 1987 *Phys. Rev. B* **36** 4630
- [9] Turchi P E A, Stocks G M, Butler W H, Nicholson D M and Gonis A 1988 *Phys. Rev. B* **37** 5982
- [10] Akai H <http://sham.phys.sci.osaka-u.ac.jp/kkr/>
- [11] Akai H 1989 *J. Phys.: Condens. Matter* **1** 8045
- [12] Terakura K, Oguchi T, Mohri T and Watanabe K 1987 *Phys. Rev. B* **35** 2169