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First-principles calculations of total energy for Cu–Pd disordered alloys

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Abstract. A method of calculating the total energy for disordered alloys is presented. A formula for the potential in the self-consistent Korringa–Kohn–Rostoker coherent-potential approximation is also given by using the muffin-tin approximation after the variation of the total energy is made. This method was applied to Cu–Pd alloys. The numerical results indicate that the disordered state is stable over the whole concentration range of Pd. This agrees with experiments.

1. Introduction

The Korringa–Kohn–Rostoker coherent-potential approximation (KKR-CPA) is very useful to study disordered alloys (Ehrenreich and Schwartz 1976, Faulkner 1982). The electronic structure for a number of disordered alloys, for example Cu–Zn (Bansil and Ehrenreich 1974), Cu–Ni (Stocks *et al* 1978, Faulkner and Stocks 1980), Ag–Pd (Pindor *et al* 1980, Stocks and Winter 1982), Ni–Pd (Akai 1982), Cu–Pd (Rao *et al* 1984, Winter *et al* 1986), Cu–Pt and Cu–Au (Ginatempo *et al* 1990), has been clarified over the past two decades. Moreover, the total energy of the ground state for disordered alloys has been obtained for some alloy systems (Sigli *et al* 1986, Johnson *et al* 1990) and the KKR-CPA calculation has been applied to the study of the alloy phase diagram (Gyorffy *et al* 1989, Gonis *et al* 1991). In those self-consistent KKR-CPA calculations, the muffin-tin potential is derived by the variation principle based on the density-functional theory (Hohenberg and Kohn 1964). The muffin-tin potential is not, however, determined uniquely, because the potential is approximated to be a constant in the interstitial region outside the muffin-tin sphere. A formula for the muffin-tin potential was given by Janak (1974). Janak's formula has often been used in first-principles calculations. The variation of the total energy with respect to the electron density $\rho(r)$ is usually achieved after the muffin-tin approximation is used for the total-energy expression in this formula. If the muffin-tin approximation is made after the variation, the result is different. The former gives the minimum of the total energy approximated by the muffin-tin sphere exactly, and the latter gives the minimum of the exact energy approximately.

In disordered alloys, the potential procedure is more complicated, because the configuration of atoms is not determined uniquely. Then, based on the single-site approximation, it is necessary that the effects of other nuclei and electrons outside a lattice site are approximated by the average over all configurations of atoms in disordered alloys. Such an approximation introduces a freedom of choice of the electron density in the

interstitial region, which is constant in the muffin-tin approximation. In a monatomic metal whose atomic number is Z , the interstitial electron density is defined by

$$\rho_0 = \frac{1}{\Omega_0} \left(Z - \int_S d^3r \rho(r) \right) \quad (1.1)$$

where Ω_0 is the volume of the interstitial region per atom and S denotes the integral in the muffin-tin sphere. In a substitutional disordered binary alloy, A and B atoms are assumed to occupy regular lattice sites randomly with probability X_A and X_B respectively, where $X_A + X_B = 1$. Then, the interstitial electron density for a site is considered to be ρ_0^A if the site is occupied by an A atom or ρ_0^B if the site is occupied by a B atom. Put another way, the electrons outside the muffin-tin spheres are considered not to belong to an atom only. Then the interstitial electron density is given by $X_A \rho_0^A + X_B \rho_0^B$. Both methods satisfy charge neutrality. Johnson *et al* (1990) calculated the total energies of Cu–Ni alloys with the latter formula and obtained good results. We have calculated the total energies of Cu–Pd alloys with the same method as used by them. The Cu–Pd alloy system forms solid solutions at any concentration of Pd. The numerical results, however, show that the disordered state is unstable in the Cu-rich phase. This is not in agreement with the experiments. Since the KKR-CPA is a single-site approximation, the electron states are calculated as for a neutral atom embedded in an effective medium. Namely, the wavefunctions of electrons are normalized in the Wigner–Seitz cell. If charge neutrality for each atom is not demanded in the estimation of the potential, that is not a self-consistent calculation.

In this paper, a formula is derived with the interstitial electron density which satisfies charge neutrality on each atomic site. Moreover, the variation is achieved before the muffin-tin approximation in the deviation, because otherwise an unreasonable term appears. This method was applied to Cu–Pd disordered alloys. In this paper, the Rydberg atomic unit is used.

The remainder of the paper takes the following form. In section 2 the formalism of the total energy and the potential is described with the approximation mentioned above. In section 3 the numerical technique used in this work is shown. The numerical results and discussion are presented in section 4. We summarize our results in section 5.

2. Formalism

The total energy of a solid is given by

$$E = T + U + E_{xc} \quad (2.1)$$

where T , U and E_{xc} are the kinetic energy, the potential energy and the exchange–correlation energy respectively. The formulation of the total energy for a monatomic solid is discussed in detail with the muffin-tin approximation by Janak (1974). For substitutional binary alloys, the total energy is estimated with the average over the configurations of atoms.

The kinetic energy is given by

$$T = \left\langle \sum_i \epsilon_i - \int d^3r V(r) \rho(r) \right\rangle \quad (2.2)$$

where the first term in the bracket means summation of the eigenenergy values over all electron states. These states are divided into core states and valence states. The core states

are bound near the nuclei. Then the contribution of core states is given by the average of the eigenenergy of core states in each atom. The valence state electrons, however, are not bound by an atom. The energy of valence states is given by the band-energy calculation, which is achieved by the KKR-CPA method for disordered alloys. In the second term of equation (2.2), $V(r)$ and $\rho(r)$ are the effective one-electron potential and the electron density, which is given by

$$\rho(r) = -\frac{2}{\pi} \text{Im} \int_{-\infty}^{E_F} dE G(r, r, E) \quad (2.3)$$

where $G(r, r, E)$ is a Green function. The integral in (2.2) is estimated over the whole crystal. In the muffin-tin approximation, the crystal is divided into the muffin-tin spheres and the interstitial region. The potential $V(r)$ is replaced by the spherical average in the sphere and a constant value in the interstitial region. Moreover, the constant value is often given as zero for convenience. Then the integral is replaced by a summation of the integrals for each muffin-tin sphere.

The potential energy is given by

$$U = \left\langle -2 \sum_i Z_i \int d^3r \frac{\rho(r)}{|r - R_i|} + \int \int d^3r d^3r' \frac{\rho(r)\rho(r')}{|r - r'|} + \sum_{i \neq j} \sum \frac{Z_i Z_j}{|R_i - R_j|} \right\rangle \quad (2.4)$$

where Z_i and R_i denote atomic number and atomic position of the i th atom, respectively. The electron density $\rho(r)$ is replaced by the spherical average in the muffin-tin sphere and a constant value ρ_0^i , which depends on the i th atom, in the interstitial region under the muffin-tin approximation. These are related according to

$$\rho_0^i = \frac{1}{\Omega_0} \left(Z_i - 4\pi \int_0^{R_m} dr r^2 \rho(r) \right) \quad (2.5)$$

where R_m and Ω_0 are the muffin-tin radius and the volume of an interstitial region, respectively, for each atom. They satisfy the following relation

$$\Omega = \Omega_0 + \frac{4}{3}\pi R_m^3 \quad (2.6)$$

where Ω is the volume of the Wigner-Seitz cell that is occupied by an atom. In this work, the Wigner-Seitz cell is approximately replaced by a sphere, the volume of which is the same as that of the other sphere. All muffin-tin spheres are also assumed to have the same volumes. Then equation (2.4) is represented by

$$\begin{aligned} \frac{1}{N} U = & \left\langle 2(4\pi)^2 \int_0^{R_m} dr r \rho(r) \int_0^r dr' r'^2 \rho(r') - 8\pi Z_i \int_0^{R_m} dr r \rho(r) \right\rangle \\ & - C_1 \frac{(\rho_0 \Omega_0)^2}{2a} + C_2 ((\rho_0^i - \rho_0)^2) a^5 \end{aligned} \quad (2.7)$$

where

$$C_1 = \frac{2\Omega^2}{\Omega_0^2} A - \frac{8\pi}{\Omega_0} a R_m^2 - \frac{2(4\pi)^2}{5\Omega_0^2} a R_m^5 \quad (2.8)$$

$$C_2 = \frac{1}{a^5} \left(\int_{\Omega_0} d^3r \int_{\Omega_0} d^3r' \frac{1}{|r - r'|} - 2 \int_{\Omega_0} d^3r \frac{\Omega_0}{r} \right) \quad (2.9)$$

$$\rho_0 = \langle \rho_0^i \rangle \quad (2.10)$$

and a is the lattice constant. The constant A in (2.8) is defined by

$$\frac{A}{a} = \frac{1}{\Omega} \int d^3r \frac{1}{r} - \sum_i \frac{1}{R_i}. \quad (2.11)$$

The constants C_1 , C_2 and A depend on crystal structure only. C_1 and A are calculated by Janak (1974) and Coldwell-Horsfall and Maradudin (1960) respectively. The last term in equation (2.7) is a correction due to a self-correlation for the average. Though the necessity of such a correction is pointed out by Johnson *et al* (1990), our result is slightly different from theirs. Our results are obtained by using the respective interstitial electron densities necessarily. The coefficients C_1 and C_2 are tabulated in table 1 using the Wigner-Seitz sphere approximation. The values of C_2 are less than those of C_1 for cubic crystals as shown in table 1. The contribution of the term with C_2 , however, is not so small. The results of the total-energy calculation for $\text{Cu}_{0.5}\text{Pd}_{0.5}$ alloy with the C_2 term and those without it are shown in figure 1.

Table 1. Values of C_1 (Janak 1974) given by (2.8), C_2 given by (2.9) and C_3 given by (2.18) (unit, Rydberg).

Lattice	C_1	C_2	C_3
sc	3.116 685	-0.417 966 49	3.683 203 6
bcc	4.085 521	-0.056 369 73	4.408 699 1
fcc	4.832 066 4	-0.011 489 07	5.458 768 3

The exchange-correlation energy is given by

$$E_{xc} = \left\langle \int d^3r \rho(r) \epsilon_{xc}[\rho(r)] \right\rangle \quad (2.12)$$

in the local-density approximation (Kohn and Sham 1965) where ϵ_{xc} is given by Perdew and Zunger (1981). The integral region is divided into Wigner-Seitz cells. Then, the average of the energy is replaced by the average of the integral over each cell in which either an A or B atom exists. The electron density outside the muffin-tin sphere, however, is arbitrary whether ρ_0 or ρ_0^i . In this work, ρ_0^i is used because this choice has led to the lower total energy as a result of the numerical calculations.

The potential and the electron density on one atom site are different from those on another site in disordered alloys, even if those sites are occupied by the same atoms, because the surroundings are not the same site by site. In the KKR-CPA, they are approximately replaced by ones for an atom embedded in an effective medium. They should satisfy the Kohn-Sham equation in the density-functional theory (DFT) in order to estimate the total energy of the ground state. In the DFT, the potential of the i th site is given by the variation of the energy with respect to the electron density of the i th site as follows:

$$V_i(r) = \delta U / \delta \rho_i(r) + \delta E_{xc} / \delta \rho_i(r). \quad (2.13)$$

The first term is obtained by

$$\frac{\delta U}{\delta \rho_i(r)} = -2 \sum_i Z_i \frac{1}{|r - R_i|} + 2 \int d^3r' \frac{\rho_i(r')}{|r - r'|} \quad (2.14)$$

using (2.3). The exchange-correlation term is given by

$$\delta E_{xc}/\delta \rho_i(r) = \mu_{xc}[\rho_i(r)] \quad (2.15)$$

where μ_{xc} is given by Perdew and Zunger (1981). In order to make the potential zero in the interstitial region, the average of the potential in the interstitial region is subtracted. The Wigner-Seitz cell can be replaced approximately with a sphere. The contribution of the potential due to other nuclei is described with Legendre polynomials as

$$\sum_i' \frac{1}{|r - R_i|} = \sum_l \sum_i' \frac{1}{R_i} \left(\frac{r}{R_i}\right)^l P_l(\cos \theta_i) \quad (2.16)$$

for $R_i > r$. For crystals with cubic symmetry, the terms with $l = \text{odd}$ and $l = 2$ vanish. Since $R_i > r$, the terms with $l > 4$ may be neglected. Then, the term with $l = 0$ only is left. The potential is obtained as follows:

$$V_i(r) = \begin{cases} 0 & (r > R_m) \\ -\frac{2Z_i}{r} + 8\pi \int_0^r dr' \left(\frac{r'^2}{r} - r'\right) \rho_i(r') + 8\pi \int_0^{R_m} dr r \rho_i(r) & (2.17) \\ +C_3 \frac{\rho_0^i \Omega_0}{a} + \mu_{xc}[\rho_i(r)] - \mu_{xc}[\rho_0^i] & (r < R_m) \end{cases}$$

where

$$C_3 = a \left(\frac{\Omega}{\Omega_0^2} 4\pi(R_s^2 - R_m^2) + \frac{(4\pi)^2}{15\Omega_0^2} (R_s^5 - R_m^5) - \frac{4\pi R_m^2}{\Omega_0} \right) \quad (2.18)$$

which is tabulated in table 1, is different from C_1 given by (2.8). If the variation method is used after the muffin-tin approximation to obtain the potential, the coefficient of the last term is not C_3 but C_1 , which is similar to Janak's formula.

3. Numerical consideration

First, self-consistent field (SCF) KKR-CPA equations are solved with the potential formula given by (2.17). The electron density of the valence states is calculated from (2.3) with the complex energy method (Johnson *et al* 1984), because the Green function is smooth as a function of the energy of which the imaginary part is large. The integral path on the complex energy plane is shown in figure 2. The lowest energy E_s of the real axis has been chosen to be -0.2 Ryd in the present work. The choice of E_s is arbitrary between the core state and the valence one. The imaginary part γ of the path is 0.5 Ryd. The upper real part of the path is the Fermi energy that is determined every iteration, which is necessary to solve the equations self-consistently. On that path, 63 energy points are used to estimate the integral. The electron density due to core electrons is calculated from the Schrödinger equation for bound states every iteration.

Secondly, the CPA equations are solved at each energy point for every self-consistent iteration. Then, the effective scattering amplitude t_e is estimated with the integral

$$\int_{\text{IBZ}} d^3k (t_e - B_k)^{-1} \quad (3.1)$$

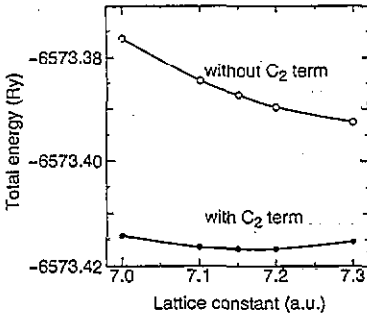


Figure 1. Effect of the correction term C_2 on the total energy of $\text{Cu}_{0.5}\text{Pd}_{0.5}$ disordered alloy.

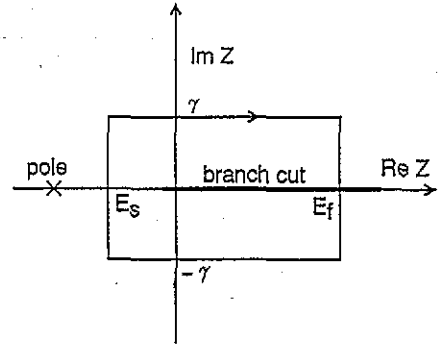


Figure 2. An integral path on the complex energy plane.

of k -space where B_k is the structure constant. Both t_e and B_k are matrices with respect to the angular momentum quantum number. After investigating some k -integral methods, for example the special-point method (Chadi and Cohen 1973), the special-direction method (Bansil 1975, Fehner and Vosko 1976) and the prism method (Stocks *et al* 1979), the following method has been used in the present calculation. The k -integral is calculated with the special-point method. The number of k -points needs to be 10 far away from the real axis and 60 near the real axis to make the k -integral converge numerically. Once the effective scattering amplitude t_e is determined with the special-point method, the scattering T matrix for an A or B atom embedded in an effective medium is calculated with Lloyd's (1967a, b) formula. In this calculation, the effective scattering amplitude t_e is estimated again by the prism method for a k -integral near the real axis, because the scattering T matrix is sensitive to the k -integral, though a determination of the scattering amplitude is not. In the prism method (Stocks *et al* 1979), the $1/48$ reduced Brillouin zone is divided into 64 pyramids. In each pyramid, the one-dimensional integral is calculated from the values of the integrand at 30 k -points with interpolation of the numerator and the denominator of the integrand, respectively, because they have no singular points except free electron poles, which are avoided by multiplying by the factor $(k^2 - E_{\text{free}})$, though the integrand has some singular points. Via this method, the k -integral is estimated with an accuracy of about 1 part in 10^6 . Thus, the present calculation has been made to an accuracy of about 0.1 mRyd as for the total energy.

Finally, the electron density of states is defined by

$$g(E) = -\frac{2}{\pi} \text{Im} \int_{\Omega} d^3r G(r, r, E) \quad (3.2)$$

for a real energy E . It takes a lot of effort to solve the KKR-CPA equations for real energies, because many k -points are needed to make the k -integral, given by (3.1), converge. In the present work, the densities of states have been estimated for complex energies $E + i\gamma$ instead of real energies E . The imaginary part γ , which is 0.1 mRyd in this work, should be small enough to give similar results to those for real energies.

4. Results and discussion

The electronic structure and the total energy were calculated with SCF KKR-CPA for $\text{Cu}_{1-x}\text{Pd}_x$ disordered alloys ($x = 0, 0.05, 0.25, 0.5, 0.75, 0.9, 1.0$). The equilibrium lattice constants,

at which the total energies are minimum, are shown in figure 3 (full circles). The open circles are obtained experimentally by Jones and Sykes (1939). The difference of the lattice constants is a few per cent between the calculation and the experiments. Both the calculated result and the experimental one, however, indicate that the dependence of the lattice constant on Pd concentration is different between Cu-rich alloys and Pd-rich alloys. Then, Cu-Pd alloys do not obey Vegard's law. The differences between calculations and experiments in Pd-rich alloys are considered to be caused by the sensitivity of the Fermi energy, which is put in the energy band.

The heats of formation of alloys, as follows

$$\Delta H = E_{\text{tot}}(\text{Cu}_{1-x}\text{Pd}_x) - (1-x)E_{\text{tot}}(\text{Cu}) - xE_{\text{tot}}(\text{Pd}) \quad (4.1)$$

are shown in figure 4. A term due to a pressure in an enthalpy may be neglected at normal pressure. The heat of formation is negative over the whole concentration of Pd. Then, the disordered state is more stable than the segregated state to two phases in Cu-Pd alloys. The concentration of Pd at which the heat of formation is minimum is not 50% but 40%. Our results agree with the experimental results (Hultgren *et al* 1973), shown by the broken curve in figure 4, with respect to these viewpoints, though our results are lower than experimental ones.

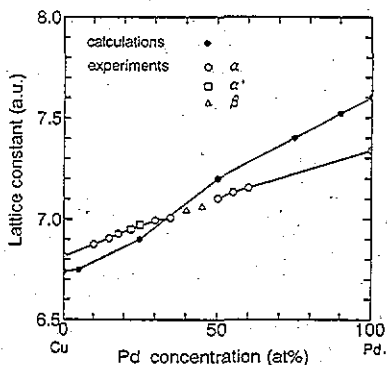


Figure 3. Lattice constants of Cu-Pd alloys by calculations (full circles) and experiments (open symbols) by Jones and Sykes (1939).

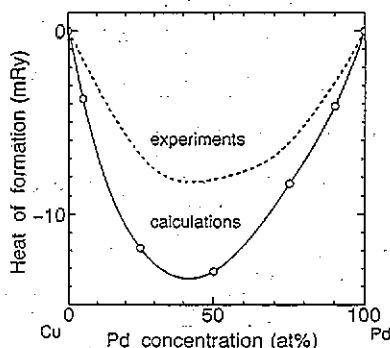


Figure 4. Heats of formation of Cu-Pd alloys by calculations (full curve) and experiments (broken curve) by Hultgren *et al* (1973).

The densities of states (full curve) are shown with the local densities of states for Cu (dotted curve) and Pd (broken curve) in figure 5. Our results agree with those of Winter *et al* (1986) on the whole. At low concentration of Pd, the states of Pd are spread out by d states of Cu. The peak at the centre of the energy band of Pd, which is due to d_e states, increases with Pd concentration. This peak is considered to be resonant with d_e states of Cu. Especially, the peak is sharp at Cu_{0.25}Pd_{0.75}. The density of states at the Fermi energy is related to the electron specific heats. Our results (full circles) and experimental results (open circles) by Sato *et al* (1970) are shown in figure 6. Our results agree with those of Winter *et al* (1986) (broken curve), calculated with SCF-KKR-CPA. The difference between calculations and experiments is considered to be due to the electron-phonon interaction.

Finally, the numbers Z^{in} of electrons in the muffin-tin sphere for Cu (full circles) and Pd (open circles) are shown in figure 7. The number of electrons increases with Pd

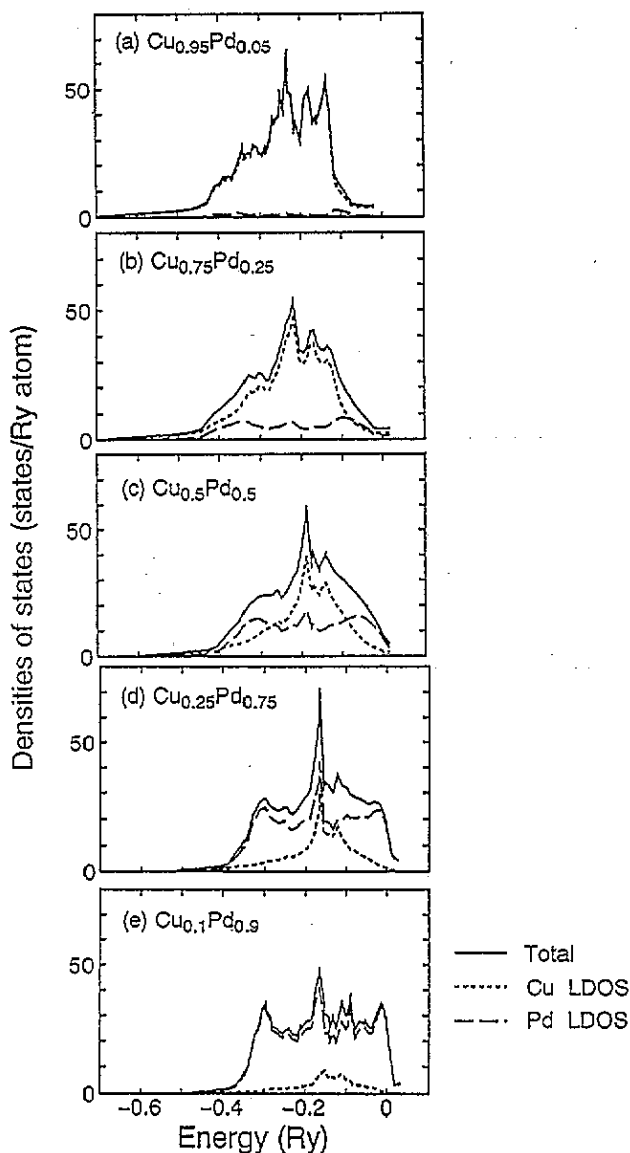


Figure 5. Total densities of states (full curve) and local densities of states of Cu (dotted curve) and Pd (broken curve) for (a) $\text{Cu}_{0.95}\text{Pd}_{0.05}$, (b) $\text{Cu}_{0.75}\text{Pd}_{0.25}$, (c) $\text{Cu}_{0.5}\text{Pd}_{0.5}$, (d) $\text{Cu}_{0.25}\text{Pd}_{0.75}$ and (e) $\text{Cu}_{0.1}\text{Pd}_{0.9}$.

concentration in both sites. Electrons are considered to transfer from the Pd site to the Cu site. Triangles denote Winter *et al*'s (1986) results. Compared with them, our results indicate that the charge transfer occurs more remarkably. Johnson *et al* (1990) pointed out that charge transfer is ignored by the use of charge neutrality for each atom site. The charge transfer, however, should be discussed with respect to the electrons in a muffin-tin sphere, because the interstitial electrons are not bound by an atom. Under this consideration, the charge transfer is recognized even if the charge neutrality for each atom site is used. Moreover, the cluster KKR-CPA (Takano *et al* 1991), which is a many-sites approximation,

is needed if the charge transfer is estimated more exactly. The total-energy calculation with the cluster KKR-CPA will require more effort.

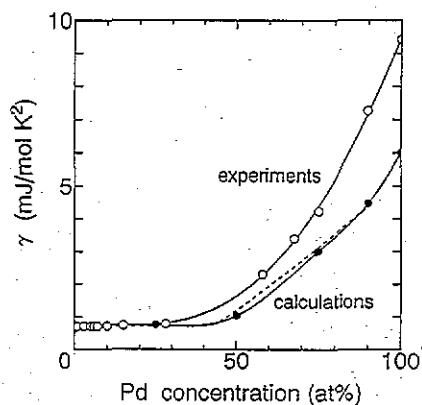


Figure 6. Electron specific-heat coefficients for Cu-Pd alloys by our calculation (full circles), Winter *et al*'s (1986) (broken curve) and experiments (open circles) by Sato *et al* (1970).

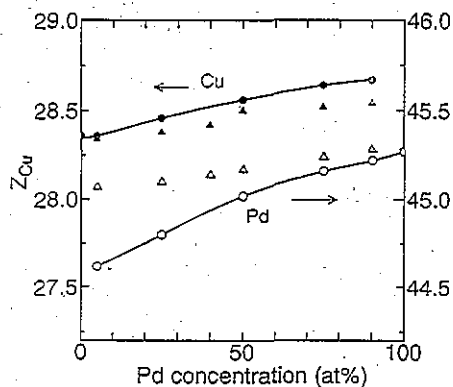


Figure 7. Number of electrons in the muffin-tin spheres of Cu (full symbols) and Pd (open symbols) in Cu-Pd alloys. Circles are our work; triangles are Winter *et al*'s (1986) results.

5. Summary

The total energy was formulated in the muffin-tin approximation for disordered alloys. In this formula, the correction term is derived. This term is considered to take an important part in the total-energy calculation. The potential is derived by the variation principle. In the present work, the variation was made before the muffin-tin approximation was used. This formula was applied to Cu-Pd alloys provided that charge neutrality for each atom is assumed. As a result, the Cu-Pd alloy system forms a solid solution over the whole concentration of Pd and is not governed by Vegard's law. Moreover, it is considered that electrons transfer from the Pd site to the Cu site and d states of Cu and Pd make a resonance. Such results agree with experiments, and so the formula presented in this paper is reasonable. This formula is expected to give good results for other alloy systems.

As discussed previously, the formation energy of disordered alloys is sensitive to the muffin-tin approximation and charge neutrality. In particular, this tendency is strong in disordered alloys because of the difference of the interstitial charge densities. The density of states, however, is insensitive to them even for disordered alloys. The muffin-tin approximation should be made with care in order to discuss the formation energy of disordered alloys.

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