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EFFECT OF THERMAL FLUCTUATIONS ON THE ELECTRONIC DENSITY OF STATES IN DISORDERED BINARY ALLOYS

I. CPA for Off-Diagonal Randomness

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I. CPA for Off-Diagonal Randomness
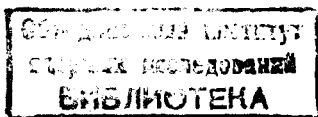
Summary

The electron-phonon interaction in binary alloys is studied on the basis of a tight-binding model Hamiltonian including diagonal and off-diagonal randomness due to substitutional and thermal disorder. The stochastic model specialized to the additive limit is treated within the adiabatic approach by using an extended coherent potential approximation. The random scattering potentials fluctuate thermally according to Gaussian distributions. A set of integral equations for the electronic self-energy is derived. The temperature dependence of the density of states is expressed in terms of four fluctuation parameters.

1. INTRODUCTION

The aspect of thermal disorder contributes to a better understanding of the electronic properties in substitutionally disordered system such as binary alloys. Dealing with the effect of thermal fluctuations one usually starts considering the motion of the electron in the field of fluctuating potentials due to lattice vibrations. In other words, it is necessary to investigate the behaviour of the electron influenced by the combined effects of the randomness and the electron-phonon interaction. The picture of a static random lattice seems to be reasonable within the scope of the adiabatic approximation.

Such a problem was treated in the coherent potential approximation (CPA) by Chen et al.[1] and applied to calculate the electronic density of states and the d.c.conductivity. However, these calculations are restricted to the case of diagonal (substitutional and thermal) disorder in the tight-binding model Hamiltonian. For a similar type of thermal disorder in the case of the exciton-phonon interaction, Sumi[2] proposed the CPA for studying the exciton density of states and optical absorption spectra. The

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small-polaron approach to the problem of electron-phonon interaction was used by Böttger and Bryksin[3] to develop a theory of optical intraband absorption in disordered systems. Moreover, for example, Brenig et al.[4] and Čápek [5] investigated the electron-phonon coupling in structurally disordered systems in the context of the phonon-assisted hopping conductivity.

In this paper we start from a model Hamiltonian with random diagonal and off-diagonal elements caused by substitutional and thermal disorder in the binary alloy. The type of disorder is specialized by assuming additive conditions for the transfer elements. In particular, Fukuyama et al.[6] considered this additive limit in the absence of thermal disorder.

Following ideas of [1] , we can derive a set of self-consistency relations to determine the momentum-dependent coherent potential as a quadratic form of the lattice structure factor. The assumptions and approximations we use correspond to a single site approach. The formalism obtained here in the presence of electron-phonon interaction can be regarded as a natural extension of the modified CPA which was represented in[7] .

2. MODEL FOR SUBSTITUTIONAL AND THERMAL DISORDER

The treatment of the electron motion in substitutionally disordered $A_c B_{1-c}$ alloys is based upon a tight-binding model including thermal disorder. The Hamiltonian is assumed to have the form

$$H = H_e + H_{eph} , \qquad (1)$$

where

$$H_e = \sum_n \epsilon_n a_n^+ a_n + \sum_{\substack{n,m \\ (n \neq m)}} h_{nm} a_n^+ a_m , \qquad (2)$$

$$H_{eph} = \sum_{n,m} \sum_s (\gamma_{nm}^{(s)} b_s + (\gamma_{mn}^{(s)})^* b_s^+) a_n^+ a_m . \qquad (3)$$

Here $a_n^+ (a_n)$ and $b_s^+ (b_s)$ are creation (annihilation) operators for an electron in the Wannier state at lattice site n and for a phonon with the quantum number s, respectively. The s summation is extended over all $3N$ normal modes of lattice vibrations, where N lattice sites are randomly occupied by atoms A or B. The atomic energies ϵ_n, the hopping integrals h_{nm} as well as the matrix elements $\gamma_{nm}^{(s)}$ of the electron-phonon interaction are taken to be configuration dependent. This dependence is denoted by ϵ_n^ν, $h_{nm}^{\nu\mu}$, $\gamma_n^{(s)\nu}$ (for the diagonal element $\gamma_{nn}^{(s)\nu\nu}$) and $\gamma_{nm}^{(s)\nu\mu}$ or equivalently by ϵ^ν, $h^{\nu\mu}$, $\gamma^{(s)\nu}$ and $\gamma^{(s)\nu\mu}$; here the superscript $\nu(\mu)$ refers to the atomic species (ν , $\mu =$ A,B) located at site $n(m)$. Only nearest-neighbour (n.n.) transfer elements h_{nm} and $\gamma_{nm}^{(s)}$ are considered.

The electron-phonon interaction Hamiltonian H_{eph} is treated within the adiabatic approximation. Then it is possible to suppress the ionic motion in (3), i.e., the electron-phonon scattering can be reduced to a random lattice problem. In other words, the electron-phonon interaction can be re-

placed by an interaction of the electron with a time-independent c-number field with diagonal and off-diagonal randomness. This static approximation is equivalent to the condition of elastic electron-phonon scattering.

In order to specialize the type of off-diagonal randomness in the one-electron Hamiltonian H_e, we choose the additive condition[6,7]

$$h^{AB} = \frac{1}{2}(h^{AA} + h^{BB}),\qquad (4)$$

where $h^{\nu\mu}$ stands for the hopping energy h_{nm} between the atom of type ν located at $\vec{R}_n$ (position vector of site n) and the neighbouring atom of type μ at $\vec{R}_m$. Analogously, the off-diagonal (nonlocal) matrix elements $\gamma^{(s)}_{nm}$, which characterize the phonon scattering of the electron accompanied with simultaneous electron transfer, are assumed to satisfy the condition

$$\gamma^{(s)AB} = \frac{1}{2}(\gamma^{(s)AA} + \gamma^{(s)BB}).\qquad (5)$$

This condition can be replaced in our following treatment by a weaker one.

In the case (4) and (5) the general Hamiltonian (1) can be rewritten as

$$H = H_e^B + \sum_n[(E_n + \Theta_n)a_n^+ a_n + \sum_{\substack{m \\ (m \neq n:\, n.n.)}} (h_n + \theta_n)(a_n^+ a_m + a_m^+ a_n)]$$

$$= H_e^B + \sum_n V_n,\qquad (6)$$

where H_e^B represents the one-electron Hamiltonian (2) for a perfect B crystal. According to whether on A or B atom occupies the n-th site, the random part V_n is configuration dependent in the following way:

1. The variable E_n takes one of two values $(\epsilon^A - \epsilon^B)$ or zero.

2. The operator Θ_n due to the local electron-phonon interaction has the form[1]

$$\Theta^\nu = \sum_s (\gamma^{(s)\nu} b_s + (\gamma^{(s)\nu})^* b_s^+),\qquad (\nu = A, B)\qquad (7)$$

where Θ^ν means Θ_n^ν.

3. The variable h_n is equal to either $(h^{AB} - h^{BB})$ or zero.

4. The operator θ_n, which results from the nonlocal electron-phonon coupling, is written as

$$\theta^\nu = \frac{1}{2}\sum_s (\gamma^{(s)\nu\nu} b_s + (\gamma^{(s)\nu\nu})^* b_s^+),\qquad (\nu = A, B)\qquad (8)$$

where θ^ν stands for θ_n^ν.

In comparison with (5), the weaker assumption to derive the Hamiltonian (6) is

$$\theta^{AB} = \frac{1}{2}(\theta^A + \theta^B),\qquad (9)$$

where

$$\theta^{AB} = \sum_s (\gamma^{(s)AB} b_s + (\gamma^{(s)AB})^* b_s^+).\qquad (10)$$

In addition, there is position dependence concerning Θ_n and θ_n. The phonon operators Θ_n and θ_n depend on the phonon coordinates which are determined by the special set of

phonon modes associated with a particular alloy configuration. The Θ_n term in (6) used in adiabatic approximation can be interpreted as adiabatic potential at site n due to local deformation of the lattice during thermal vibrations. Moreover, the phonon-assisted transition in θ_n represents the change of the electron-hopping integral by lattice deformation.

3. CPA WITH $\vec{k}$-DEPENDENT SELF-ENERGY

Introducing the one-particle Green operator

$$G(z) = (z - H)^{-1}, \qquad (11)$$

we must average over all atomic distributions in order to find macroscopic properties of the disordered system. The adiabatic picture allows one to carry out successively two independent procedures of averaging /1/. In the first one, the average over all possible positions of the ions in a particular alloy configuration is performed (denoted by $<...>_{ph}$). In the second one, we average over all configurations (indicated by $<...>_c$).

The averaged Green operator (11) related to the Hamiltonian (6) is written as

$$\ll G >_{ph} >_c = (z - H^B_e - \Sigma)^{-1}, \qquad (12)$$

and has in Bloch representation the form

$$\ll G(z) \gg_{\vec{k}} = \mathcal{G}_{\vec{k}}(z) = [z - \epsilon^B - h^{BB} s(\vec{k}) - \Sigma(\vec{k}, z)]^{-1}, \qquad (13)$$

where the indices for the double average are

dropped. The nearest-neighbour structure factor of the lattice is defined by

$$s(\vec{k}) = \sum_{\substack{m \\ (m \neq n : n.n.)}} e^{i\vec{k}(\vec{R}_m - \vec{R}_n)}. \qquad (14)$$

The Green's function $\mathcal{G}_{\vec{k}}(z)$ and the electronic self-energy $\Sigma(\vec{k}, z)$ in (13) reflect the property of translational invariance due to the average.

To calculate the self-energy $\Sigma(\vec{k}, z)$, we use the technique developed in /7/ for the case of additive off-diagonal disorder. This case is given in the Hamiltonian (6) which is divided into the unperturbated part H^B_e and the random additive operator $V = \sum_n' V_n$, where the single-site potentials V_n are not localized on the corresponding sites, i.e., the individual potentials are of finite range.

The CPA self-energy $\Sigma(\vec{k}, z)$ is described by the ansatz /7/

$$\Sigma(\vec{k}, z) = \sigma_0(z) + 2\sigma_1(z) s(\vec{k}) + \sigma_2(z) s^2(\vec{k}), \qquad (15)$$

where $\sigma_\ell(z)$ ($\ell = 0, 1, 2$) are complex variables to be determined self-consistently. The $\vec{k}$-dependence of the self-energy is caused by the off-diagonal disorder.

Using the single-site approximation, the self-consistency requirement resulting from the multiple scattering theory may be written in Bloch representation as

$$\ll <\vec{k}| T_n |\vec{k}'> \gg = 0, \qquad (16)$$

where the T_n-operator related to the single scattering centre n is /8/

$$T_n = (V_n - \Sigma_n)[1 - \ll G \gg (V_n - \Sigma_n)]^{-1} .. \qquad (17)$$

Here the single-site contributions of the potential in (6) are given by

$$\langle \vec{k} | V_n | \vec{k}' \rangle = \frac{1}{N} e^{-i(\vec{k}-\vec{k}')\vec{R}_n} \{(E_n + \Theta_n) + (h_n + \theta_n)[s(\vec{k}) + s(\vec{k}')]\} , \qquad (18)$$

and the single-site self-energy will be chosen as

$$\langle \vec{k} | \Sigma_n(z) | \vec{k}' \rangle = \frac{1}{N} e^{-i(\vec{k}-\vec{k}')\vec{R}_n} \{\sigma_0(z) + \sigma_1(z)[s(\vec{k}) + s(\vec{k}')] + \sigma_2(z) s(\vec{k}) s(\vec{k}')\} \qquad (19)$$

corresponding with (15) by the relation $\Sigma = \sum_n \Sigma_n$. From (17) we determine with (18) and (19) the scattering matrix elements in the form

$$\langle \vec{k} | T_n(z) | \vec{k}' \rangle = \frac{1}{N} e^{-i(\vec{k}-\vec{k}')\vec{R}_n} \{t_{0n}(z) + t_{1n}(z)[s(\vec{k}) + s(\vec{k}')] + t_{2n}(z) s(\vec{k}) s(\vec{k}')\}, \qquad (20)$$

and under the constraint (16) the following CPA equations are found:

$$\ll t_{\ell n}(z) \gg = \ll \frac{a_{\ell n}(z)}{1 - D_n(z)} \gg = 0, \quad (\ell = 0,1,2) \qquad (21)$$

where

$$a_{0n}(z) = (E_n + \Theta_n - \sigma_0) + (h_n + \theta_n - \sigma_1)^2 F_2 + (E_n + \Theta_n - \sigma_0)\sigma_2 F_2 , \qquad (22)$$

$$a_{1n}(z) = (h_n + \theta_n - \sigma_1) - (h_n + \theta_n - \sigma_1)^2 F_1 - (E_n + \Theta_n - \sigma_0)\sigma_2 F_1 , \qquad (23)$$

$$a_{2n}(z) = -\sigma_2 + (h_n + \theta_n - \sigma_1)^2 F_0 + (E_n + \Theta_n - \sigma_0)\sigma_2 F_0, \qquad (24)$$

and

$$D_n(z) = (E_n + \Theta_n - \sigma_0) F_0 + 2(h_n + \theta_n - \sigma_1) F_1 - \sigma_2 F_2 - [(h_n + \theta_n - \sigma_1)^2 + (E_n + \Theta_n - \sigma_0)\sigma_2][F_1^2 - F_0 F_2] , \qquad (25)$$

with

$$F_\ell(z) = \frac{1}{N} \sum_{\vec{k}} G_{\vec{k}}(z) [s(\vec{k})]^\ell , \qquad (\ell = 0,1,2). \qquad (26)$$

For illustration, we shall use the notation

$$t_{\ell n}(z) = t_\ell(z; E_n, h_n; \Theta_n, \theta_n). \qquad (27)$$

4. AVERAGING PROCEDURE

The phonon-average in (21) means the thermodynamical average over all states of the lattice motion described by the Hamiltonian

$$H_{ph} = \sum_s \hbar \omega_s (b_s^+ b_s + \frac{1}{2}), \qquad (28)$$

where ω_s are the phonon frequencies in a given configuration. Let us express the phonon average of any function $f(\Theta_n, \theta_n)$ as

$$\langle f(\Theta_n, \theta_n) \rangle_{ph} = \iint d\eta\, d\zeta\, P_n(\eta) \tilde{P}_n(\zeta) f(\eta, \zeta), \qquad (29)$$

which is defined at temperature T in terms of the single-site distribution functions

$$P^{\nu}(\eta) = \frac{1}{\sqrt{2\pi a^{\nu}}} \exp\left(-\frac{\eta^2}{2a^{\nu}}\right), \qquad (30)$$

$$\tilde{P}^{\nu}(\zeta) = \frac{1}{\sqrt{2\pi\delta^{\nu}}} \exp\left(-\frac{\zeta^2}{2\delta^{\nu}}\right), \qquad (31)$$

with the mean-square amplitudes

$$a^{\nu} = \sum_s |\gamma^{(s)\nu}|^2 \coth\left(\frac{\hbar\omega_s}{2kT}\right), \qquad (32)$$

$$\delta^{\nu} = \frac{1}{4}\sum_s |\gamma^{(s)\nu\nu}|^2 \coth\left(\frac{\hbar\omega_s}{2kT}\right), \qquad (\nu = A, B). \quad (33)$$

Here the superscript ν refers to the type of atom at lattice site n, i.e., P^{ν} and $\tilde{P}^{\nu}$ now stand for P_n and $\tilde{P}_n$, respectively. We note two properties of the phonon averaging procedure:

1. The appearance of the product of distribution functions in (29) corresponds to the approximation that the correlation between the adiabatic potential Θ_n and the transfer quantity θ_n is neglected.
2. The Gaussian distributions (30) and (31) related to the operators (7) and (8), respectively, can be derived from the Hamiltonian (28) by using the method which has been applied /1/ to the thermal averaging of harmonic lattice vibrations with linear electron-phonon interaction.

In order to average over all configurations of the alloy, we have to consider the configurational dependence of the scattering contributions $t_\ell(z; E_n, h_n; \Theta_n, \theta_n)$, defined in

(27). Using (29) it is possible to write the self-consistency relations (21) in the more explicit form (by averaging the arbitrary index n disappears)

$$\iint d\eta\, d\zeta\, \{cP^A(\eta)\tilde{P}^A(\zeta) t_\ell(z; \epsilon^A - \epsilon^B, \frac{1}{2}(h^{AA} - h^{BB}); \eta, \zeta) +$$
$$(34)$$
$$+ (1-c)P^B(\eta)\tilde{P}^B(\zeta) t_\ell(z; 0, 0; \eta, \zeta)\} = 0, \quad (\ell = 0, 1, 2)$$

where P^{ν} and $\tilde{P}^{\nu}$ are the Gaussian distributions from (30) and (31) determined now by averaged mean-square amplitudes a^{ν} and δ^{ν} (see below). Note that the distribution functions (30) and (31) in connection with (32) and (33) are only valid for a particular alloy configuration, i.e., for a special set of phonon modes. However, the formulation of (34) requires to average the distribution functions (30) and (31) over all configurations with an atom of the type ν at site n. After having approximatively introduced the partially averaged distribution functions P^{ν} and $\tilde{P}^{\nu}$ in (34), the expressions (32) and (33) can be formally replaced by

$$a^{\nu} = \left\langle \sum_s |\gamma^{(s)\nu}|^2 \coth\left(\frac{\hbar\omega_s}{2kT}\right) \right\rangle_c^{|\nu}, \qquad (35)$$

$$\delta^{\nu} = \frac{1}{4}\left\langle \sum_s |\gamma^{(s)\nu\nu}|^2 \coth\left(\frac{\hbar\omega_s}{2kT}\right) \right\rangle_c^{|\nu}, \quad (\nu = A, B) \quad (36)$$

where the superscript "$|\nu$" indicates the fixed ν-atom at the n-th site.

In this way, the CPA equations for the random lattice problem /7/ are completed by the fact that the atomic levels and the hopping integrals fluctuate additionally with continuous distributions due to thermal vibrations of the lattice.

5. ELECTRONIC DENSITY OF STATES

In order to evaluate the self-energy parts σ_0, σ_1, σ_2 satisfying (34), we use simple input quantities. The unperturbated density of states of the pure B-band (related to H_e^B in (6)) is assumed to have the Hubbard form /8/

$$\rho_e^B(E) = \begin{cases} \frac{2}{\pi}(1-E^2)^{1/2} & \text{if } |E| \le 1, \\ 0 & \text{otherwise.} \end{cases} \qquad (37)$$

Here the half-band width w is set equal to unity, i.e., we have $h^{BB} = \frac{1}{6}$ in the case of a simple cubic lattice. The origin of the energy is chosen as $\epsilon^B = 0$. The complex quantities F_ℓ introduced by (26) can be now calculated analytically /9/ with (13) and (15) by using the residue method. This coherent Green's functions F_ℓ are obtained as

$$F_0 = 2\{\frac{1}{36\sigma_2} - i\frac{\sqrt{1-z_+^2}}{1+12\sigma_1+72\sigma_2 z_+} - i\frac{\sqrt{1-z_-^2}}{1+12\sigma_1+72\sigma_2 z_-}\}, (38)$$

$$F_1 = 12\{-\frac{(1+12\sigma_1)}{(36\sigma_2)^2} - i\frac{z_+\sqrt{1-z_+^2}}{1+12\sigma_1+72\sigma_2 z_+} - i\frac{z_-\sqrt{1-z_-^2}}{1+12\sigma_1+72\sigma_2 z_-}\}, (39)$$

$$F_2 = \frac{1}{\sigma_2}\{(z-\sigma_0)F_0 - \frac{(1+12\sigma_1)}{6}F_1 - 1\}, \qquad (40)$$

with

$$z_\pm = -\frac{(1+12\sigma_1)}{72\sigma_2} \pm \sqrt{\frac{(1+12\sigma_1)^2}{(72\sigma_2)^2} + \frac{z-\sigma_0}{36\sigma_2}}. \qquad (41)$$

The special case $\sigma_2 = 0$ leads to analogous expressions for F_ℓ.

The quantity of interest is the electronic density of states per atom defined by

$$\rho(E) = -\frac{1}{\pi}\text{Im}\, F_0(E+i0). \qquad (42)$$

The temperature dependence of σ_0, σ_1, σ_2 and ρ is investigated on the basis of the phonon parameters a^ν and δ^ν. To gain some insight into this dependence, we restrict the consideration to results obtainable without the exact knowledge of the phonon spectrum ω_s and without detailed $\gamma^{(s)\nu}$, $\gamma^{(s)\nu\nu}$. Note that a^ν and δ^ν are both proportional to kT at high temperatures, i.e., for $\frac{\hbar\omega_s}{2kT} < 1$. Let us emphasize the simplest case which is defined by $a = a^A = a^B$ and $\delta = \delta^A = \delta^B$ under the assumption that the electron-phonon interaction is independent of configurational disorder.

The parameter a at high temperatures was roughly estimated by Chen et al. /1/ using the Lindemann melting criterion on the basis of the deformational-potential theory. It has been found that the fluctuation parameter takes the values $a \approx 0.02\, T/T_m$ for a nearly-free-electron model and $a \approx 0.075\, T/T_m$ for a Ni-Cu alloy, where T_m is the melting point and the energy is expressed in units of the effective half-band width. On the

other hand, the change of the band width is also connected with thermal fluctuations related to the parameter δ. Using the same arguments as Chen et al. the ratio of the fluctuation parameters can be roughly estimated as $\delta/a \approx 2 \cdot 10^{-3}$. In another way, it is possible to get this order of δ/a for (35) and (36) by the ansatz $\gamma^{(s)\mu\nu} \propto \exp(-\lambda R)$ with a suitable choice of the radius of localization λ^{-1} and of the interatomic (n.n.) distance R. Returning to the CPA problem, the integral equations (34) can be rewritten in the dimensionless form

$$\int\limits_{-\infty}^{+\infty} d\eta \, d\zeta \, e^{-(\eta^2+\zeta^2)} \{ c \, t_\ell(z;\epsilon^A, \tfrac{1}{2}(h^{AA}-h^{BB}); \overline{\sqrt{2a^A}}\eta, \overline{\sqrt{2\delta A}}\zeta) +$$

$$\tag{43}$$

$$+ (1-c) t_\ell(z;0,0; \overline{\sqrt{2a^B}}\eta, \overline{\sqrt{2\delta^B}}\zeta) \} = 0, \quad (\ell = 0,1,2)$$

where the parameters are scaled by the half-band width w.

The formulae (43) describe both the impurity and electron-phonon scattering simultaneously and can be used to investigate the combined effect of these scattering mechanisms on the one-electron properties of the random system. In the static-alloy limit (i.e., $a = 0$, $\delta = 0$), the self-consistency relations take the algebraic form obtained in /7/. The solutions of (43) are characterized by seven parameters and can be found only numerically. Numerical results of this CPA model calculations will be reported in the subsequent paper.

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