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Electronic Structure of Alpha-Brass - Coherent-Potential Approach

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The coherent-potential approximation is used to describe the electronic spectrum of disordered alloys. Model potentials of the form used by Soven are employed to calculate the t matrices. The spectral density of states are calculated for various representations at the symmetry points Γ , X , and L , and along the Δ axis for α -Cu_{0.70}Zn_{0.30}. The results are compared with data derived from the optical studies of the alloy.

I. INTRODUCTION

The most attractive of the existing theories of the electronic structure of disordered alloys is the coherent-potential (CP) approach discussed by Soven¹ and Velický *et al.*² It has been successfully applied to a model one-dimensional alloy of δ -function potentials. In three dimensions, the procedure has been applied to a model alloy described by tight-binding wave functions. This hypothetical alloy is presumed to have constituents whose atomic wave functions are essentially identical but whose atomic eigenvalues are different. Soven³ and Velický *et al.*² have applied the CP model to this hypothetical system (they assumed a special form for the host density of states), and concluded on the basis of the results that the CP model is the best among all single-site approximations.

The object of this work is to apply the CP theory to real disordered alloys. This necessarily calls for some further approximations, but the errors thus introduced should not be more serious than those involved in conjecturing about real alloys from accurate calculations for hypothetical alloys. We chose α -brass for this calculation because a number of theoretical calculations with simpler models⁴⁻⁷ have been done for this alloy. The CP theory as presented by Soven¹ and used in this calculation neglects the presence of the short-range order. Thus, α -brass is a suitable system for application of this theory because neutron-diffraction experiments indicate that there is no short-range ordering in α -brass.⁸

The essence of the CP model is to place at each site of the alloy lattice a potential V_C , which will simulate the electronic properties of the actual al-

loy. This coherent potential V_c is a complex energy-dependent quantity. The formal Green's function G_c for the lattice of potentials V_c is given by

$$G_c = G_0 + G_0 V_c G_c, \quad (1)$$

where G_0 is the free-electron Green's function. Relative to this system, the actual alloy consists of perturbing potentials $V_1 - V_c$ and $V_2 - V_c$. The t matrix describing the scattering of an electron which is propagating according to G_c , when it encounters a potential V_s , is

$$t_s = (V_s - V_c) + (V_s - V_c) G_c t_s, \quad (2)$$

where $s = 1, 2$ denotes the type of the atom. In terms of these t matrices we have, for the actual alloy Green's function G ,

$$G = G_c + \sum_{\alpha} G_c t_{\alpha} G_c + \sum_{\alpha} \sum_{\beta \neq \alpha} G_c t_{\alpha} G_c t_{\beta} G_c + \dots \quad (3)$$

One now needs a prescription for V_c . The work of Soven and Velický *et al.* indicates that a suitable criterion for determining V_c is that, on the average, there should be no further scattering by the perturbing potentials, i. e.,

$$C_1 t_1 + C_2 t_2 = 0, \quad (4)$$

where C_1 and C_2 are atomic concentrations of atoms of types 1 and 2. With this definition, the average of Eq. (3) becomes¹

$$\langle G \rangle = G_c + \sum_{\alpha} \sum_{\beta \neq \alpha} \sum_{\gamma \neq \beta} \sum_{\delta \neq \gamma} \langle G_c t_{\alpha} G_c t_{\beta} G_c t_{\gamma} G_c t_{\delta} G_c \rangle + \dots,$$

which may be approximated as

$$\langle G \rangle \simeq G_c. \quad (5)$$

Substitution of Eq. (2) in Eq. (4) then gives the criterion for V_c as

$$u - V_c = (V_1 - V_c) G_c (V_2 - V_c), \quad (6)$$

where u is the averaged potential $C_1 V_1 + C_2 V_2$.

II. USE OF MODEL POTENTIALS

At this stage we introduce model potentials of the form discussed by Soven⁶ and Slater⁹ and replace the muffin-tin potentials at each site by potentials of the form

$$V_s(\vec{x}, \vec{x}') = \sum_L Y_L(\vec{x}) \frac{\delta(x-R)}{R^2} V_s^l \frac{\delta(x'-R)}{R^2} Y_L(\vec{x}'), \quad (7)$$

where the potential amplitude V_s^l is given by

$$V_s^l(E) = R^2 [\gamma_s^l(E) - \kappa j_l'(\kappa R) / j_l(\kappa R)], \quad (8)$$

and L is a compound subscript denoting both l and m . E is the energy $\kappa^2 = E$, and j_l, j_l' are the spherical Bessel function and its derivative, and $\gamma_s^l(E)$ is the logarithmic derivative of the actual radial wave function for angular momentum l and energy

E evaluated at the muffin-tin radius R . Inserting Eq. (7) into Eq. (6) we have

$$u^l - V_c^l = (V_1^l - V_c^l) g_l (1 - V_c^l g_l)^{-1} (V_2^l - V_c^l),$$

where $g_l = G_l(R, R)$ and $G_l(x, x')$ is the l th component in the angular momentum expansion of $G_0(\vec{x} - \vec{x}')$. We then have for V_c^l the following expression:

$$V_c^l = \frac{g_l V_1^l V_2^l - (C_1 V_1^l + C_2 V_2^l)}{g_l (C_2 V_1^l + C_1 V_2^l) - 1}. \quad (9)$$

For a potential of the form (7), the T matrix is of the form

$$T(\vec{x}, \vec{x}') = \sum_L Y_L(\vec{k}) \frac{\delta(x-R)}{R^2} t^l \frac{\delta(x'-R)}{R^2} Y_L(\vec{x}).$$

Thus the elements t_c^l of the angular momentum expansion of the t matrix corresponding to V_c are

$$t_c^l = V_c^l / (1 - V_c^l g_l). \quad (10)$$

The calculation of the spectral density of states is now straightforward. One places the t matrix corresponding to (10) at each site and works out the spectral density of states in the manner suggested by Beeby.¹⁰ We then have

$$\rho(E, \vec{k}) = -[1/(E - k^2)^2 \pi \Omega] \text{Im } T(\vec{k}), \quad (11)$$

where Im denotes the imaginary part of the quantity that follows it, and

$$T(\vec{k}) = 4\pi^2 N \sum_{LL'} Y_L(\vec{k}) Y_{L'}(\vec{k}) \{ t_l(k, k) \delta_{LL'} + [t(k, \kappa) G' (1 - G' t(\kappa, \kappa))^{-1} t(\kappa, k)]_{LL'} \}. \quad (12)$$

N is the number of sites, Ω the volume of the assembly, and $t_l(p, q)$ is given by

$$t_l(p, q) = t^l j_l(pR) j_l(qR) \quad (13)$$

with p and q being k or κ . The matrix elements of G' are given in terms of the familiar structure constants $A_{LL'}$ of the Kohn-Rostoker method by

$$G'_{LL'} = A_{LL'} + i\kappa \delta_{LL'}. \quad (14)$$

III. APPLICATION TO α -BRASS

The CP model with the use of the model potentials discussed above has been applied to α -brass. The object was to compare our results with results of other calculations using similar potentials but different schemes for finding the electronic levels. The potentials for copper and zinc were constructed by an overlap of charge densities from neighboring atoms, taking proper account of the probability of occurrence of the different types of atoms. The procedure for obtaining this potential is discussed in detail in Ref. 4. The logarithmic derivatives γ_s^l are obtained by numerically solving the radial part of the Schrödinger equation for the corresponding potential. The potential ampli-

tudes V_s^i are then obtained from Eq. (8). The other quantities required are the matrix elements for the Green's function G' . They were calculated in the way demonstrated by Ham and Segall¹¹ for the usual pure metal band calculations.

We have computed the spectral density of states for various representations at the symmetry points Γ , X , and L , and along the Δ axis for α -Cu_{0.70}Zn_{0.30}. In order to study the changes in the band structure relative to that of pure copper, we use the results given in column II of Table I of Ref. 7. These data are the results of a band calculation using the Kohn-Rostoker method. The potentials for copper and zinc in α -brass were obtained in the same manner as described in Refs. 4 and 7. The differences in the results of this and other calculations for α -brass should therefore be attributed to the differences in the models for calculating the electron states.

We have plotted in Figs. 1 and 2 the reduced spectral density of states for some states along the Δ axis. The reduced spectral density of states is defined by

$$\tilde{\rho}(E, \vec{k}) = \sum_{\vec{K}} \rho(E, \vec{k} + \vec{K}) ,$$

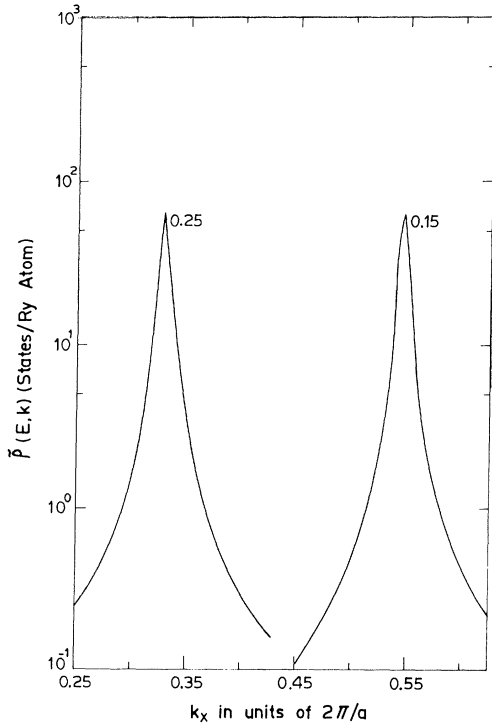


Fig. 1. The reduced spectral density of states $\tilde{\rho}(E, k)$ plotted against k_x (in units of $2\pi/a$) for Δ_2' representation in α -Cu_{0.70}Zn_{0.30}. The numbers next to the curves denote the value of the parameter $\epsilon = Ea^2/4\pi^2$, where a is the lattice parameter.

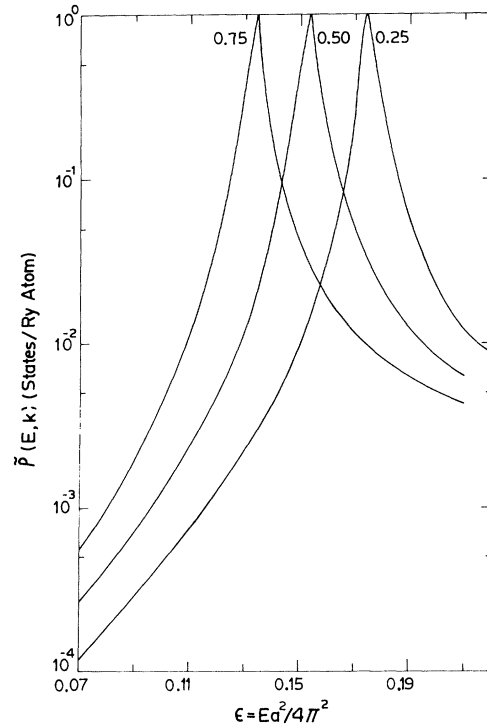


Fig. 2. The reduced spectral density of states $\tilde{\rho}(E, k)$ plotted against E (expressed in terms of $\epsilon = Ea^2/4\pi^2$) for Δ_2' representation in α -Cu_{0.70}Zn_{0.30}. The numbers next to the curves denote the value of k_x in units of $2\pi/a$.

where the summation over \vec{K} extends over the reciprocal space and \vec{k} is confined to the first Brillouin zone. The peaks in plots of $\tilde{\rho}(E, \vec{k})$ against energy are tabulated for several representations in Table I. In Fig. 1, the spectral density function is plotted against k_x (for fixed E) for Δ_2' re-

TABLE I. Peak positions (in energy measured in Ry with respect to the muffin-tin zero, $V_0 = -0.9121$ Ry) in the reduced spectral density of states in α -Cu_{0.70}Zn_{0.30} for various representations at the symmetry points Γ , X , and L , and along the Δ axis.

| Representation | Energy | Representation | Energy |
|----------------|--------|------------------------|--------|
| Γ_{25}' | 0.157 | $\Delta_2(0.25, 0.0)$ | 0.195 |
| Γ_{12} | 0.188 | $\Delta_2(0.50, 0.0)$ | 0.198 |
| X_1 | 0.085 | $\Delta_2(0.75, 0.0)$ | 0.212 |
| X_2 | 0.212 | $\Delta_2'(0.25, 0.0)$ | 0.144 |
| X_3 | 0.110 | $\Delta_2'(0.50, 0.0)$ | 0.127 |
| X_4' | 0.635 | $\Delta_2'(0.75, 0.0)$ | 0.110 |
| X_5 | 0.229 | $\Delta_3(0.25, 0.0)$ | 0.173 |
| L_1 (lower) | 0.249 | $\Delta_3(0.50, 0.0)$ | 0.224 |
| L_1 (higher) | 0.680 | $\Delta_3(0.75, 0.0)$ | 0.237 |
| L_2' | 0.465 | | |
| L_3 (lower) | 0.260 | | |
| L_3 (higher) | 0.339 | | |

TABLE II. Comparison of experimental and theoretical results for the changes in energy gap (in Ry) from Cu to α -Cu_{0.70}Zn_{0.30}.

| | $\Delta(L_1 - L_2)$ | $\Delta(X_1 - X_4)$ | $\Delta(E_F - L_3)$ |
|----------------------------|---------------------|---------------------|---------------------|
| Experimental | | | |
| Biondi and Rayne | 0.096 | | 0.026 |
| Theoretical | | | |
| AJS (virtual crystal) | 0.094 | 0.008 | 0.035 |
| Soven (average t matrix) | 0.013 | | 0.062 |
| Pant and Joshi (Ref. 7) | 0.021 | 0.021 | 0.055 |
| Present calculations | 0.167 | | 0.114 |

presentation. The half-widths of both the curves peaked at $k_x = 0.33$ and $k_x = 0.55$ (in units of $2\pi/a$, where a is the lattice parameter) are about 3% of a Brillouin-zone dimension along $\Gamma - X$, indicating appreciable Bloch character.¹² A plot of $\tilde{\rho}(E, k)$ against E (for fixed \vec{k}) is shown in Fig. 2, again for the Δ_2 representation. The numbers next to the curves are the values of k_x (in units of $2\pi/a$). We note that the curve for $k_x = 0.50$ is slightly broader than those for $k_x = 0.25$ or 0.75 , an observation which is in general agreement with Soven's conclusions for a model system.³

But there seem to be no experimental data which can be directly related to detailed form of $\tilde{\rho}(E, \vec{k})$,

and we shall limit ourselves to comparison with optical data and shall relate these to the shifts in the peak positions of $\tilde{\rho}(E, \vec{k})$ for the alloy, relative to the δ -function peaks of pure copper. The experimental information is based on the optical studies of α -brass by Biondi and Rayne.¹³ Their measurements indicate that the optical absorption edge which occurs at 2.2 eV in pure copper moves to higher energies with increasing zinc concentration, and shifts to 2.6 eV in α -Cu_{0.70}Zn_{0.30}. This is attributed to the $L_3 - E_F$ transition. The secondary absorption peak at 4.2 eV in pure copper shifts to lower energies, the reduction being 1.3 eV for 30% Zn concentration. This is attributed to $L_2 - L_1$ transition.¹⁴ Table II shows that results of the CP theory disagree with experimental data. But one must bear in mind that even for pure metals indirect transitions may be important.¹⁵ A more meaningful comparison of the various approximations could be made if additional experimental information, for example, from positron annihilation experiments, were available.

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