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Application of the Coherent Potential Approximation to
Substitutional Ternary Alloys

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Introduction The coherent potential approximation (CPA), originally proposed by Soven /1/, is now generally accepted to be the most reliable single-site theory to deal with the electronic structure of disordered alloys. In connection with the Korringa-Kohn-Rostoker multiple scattering band structure approach (KKR-CPA) it has been applied very successfully to a great number of binary alloys /2/ in the past. Recently this approach has been extended to deal with pseudobinary three-component alloys where randomness occurs on one sublattice, such as $\text{Ti}(\text{Co}_x\text{Fe}_{1-x})$ /3/ and to systems where randomness occurs on two sublattices, such as $\text{Ag}_x\text{Pd}_{1-x}\text{H}_y$ /4/. In this note the KKR-CPA equations are extended to the case of substitutional ternary alloys and results for a ternary palladium-silver-rhodium alloy are presented.

KKR-CPA equations for substitutional ternary alloys The aim of the coherent potential approximation is to find an effective medium (called the CPA medium) whose properties are as close as possible to those of the configurational average of a disordered alloy. This effective medium is determined by ignoring short-range order, i.e. assuming complete randomness and by demanding that a single atom of the alloy components embedded into the CPA medium does not change the scattering properties of the effective medium on the concentration average. As has been stated by Muñoz et al. /5/ for the analogous problem of scattering in spin-glass alloys as $\text{Ag}_x\text{Mn}_{1-x}$, where the direction of the magnetization of the Mn atoms varies from site to site, this condition is not restricted to binary alloys. By use of the so-called scattering path operator /2/ the CPA condition is given quite generally by

$$\sum_{\alpha} x_{\alpha} \tau_{\alpha}^{ii} = \tau_{\alpha}^{ii, \text{CPA}}, \quad (1)$$

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where $\underline{\tau}^{ii,\alpha}$ and $\underline{\tau}^{ii,CPA}$ are the site diagonal (site i) scattering path operators for an α -atom embedded into the CPA medium and for the CPA medium itself, respectively. All operators in this note are expressed in the angular momentum representation and "=" denotes a matrix in the quantum numbers $L = (l, m_l)$. A more useful form of (1) can be obtained by expressing $\underline{\tau}^{ii,\alpha}$ by $\underline{\tau}^{ii,CPA}$ and the single-site scattering matrix operators \underline{t}^α and \underline{t}^{CPA} for the α -atoms and the CPA medium, respectively /2/:

$$\sum_{\alpha} x_{\alpha} \left[\underline{1} + \underline{\tau}^{ii,CPA} \left((\underline{t}^{\alpha})^{-1} - (\underline{t}^{CPA})^{-1} \right) \right]^{-1} = \underline{1}, \tag{2}$$

where \underline{t}^{α} are completely determined by the potential $V^{\alpha}(\vec{r})$ within the cells of component α . The scattering path operator $\underline{\tau}^{ii,CPA}$ is coupled to \underline{t}^{CPA} via the Brillouin zone integral over the inverse KKR matrix:

$$\underline{\tau}^{ii,CPA} = V_{BZ}^{-1} \int_{V_{BZ}} d^3k \left[(\underline{t}^{CPA})^{-1} - \underline{G}(\vec{k}) \right]^{-1}, \tag{3}$$

where $\underline{G}(\vec{k})$ are the KKR structure constants /2/.

In order to solve the coupled KKR-CPA equations (2) and (3) for a ternary alloy, it is favourable to transform (2), similar to the case of a binary alloy, into

$$(\underline{t}^{CPA})^{-1} = \sum_{\alpha} x_{\alpha} (\underline{t}^{\alpha})^{-1} + \sum_{\beta, \gamma, \delta} (1 - x_{\beta}) \underline{\Delta}^{\beta} \underline{\tau}^{CPA} \underline{\Delta}^{\delta} + \underline{\Delta}^A \underline{\tau}^{CPA} \underline{\Delta}^B \underline{\tau}^{CPA} \underline{\Delta}^C, \tag{4}$$

where $\underline{\Delta}^{\alpha} = (\underline{t}^{\alpha})^{-1} - (\underline{t}^{CPA})^{-1}$, $\alpha \in \{A, B, C\}$, and (β, γ, δ) are the three cyclic permutations of (A, B, C) .

This very convenient form can only be obtained when the matrices occurring in (2) commute with each other. However, this is only the case within the non-relativistic limit, for cubic systems and $l_{max} = 2$. For all other cases (2) instead of (4) has to be used to proceed.

The coupled equations (3) and (4) can now be solved e.g. by finding a suitable guess for \underline{t}^{CPA} and solving this system of equations by iteration using the Newton-Raphson algorithm /6/. As soon as \underline{t}^{CPA} and $\underline{\tau}^{ii,CPA}$ have been determined all electronic properties of the components, as e.g. the partial densities of state, can be calculated just as in the case of a binary alloy /2/.

Results for a palladium-rhodium-silver alloy In order to demonstrate the applicability of the ternary CPA equations a calculation for the alloy $Pd_{90}Rh_5Ag_5$ was performed.

This alloy was chosen because here experimental susceptibility data for a

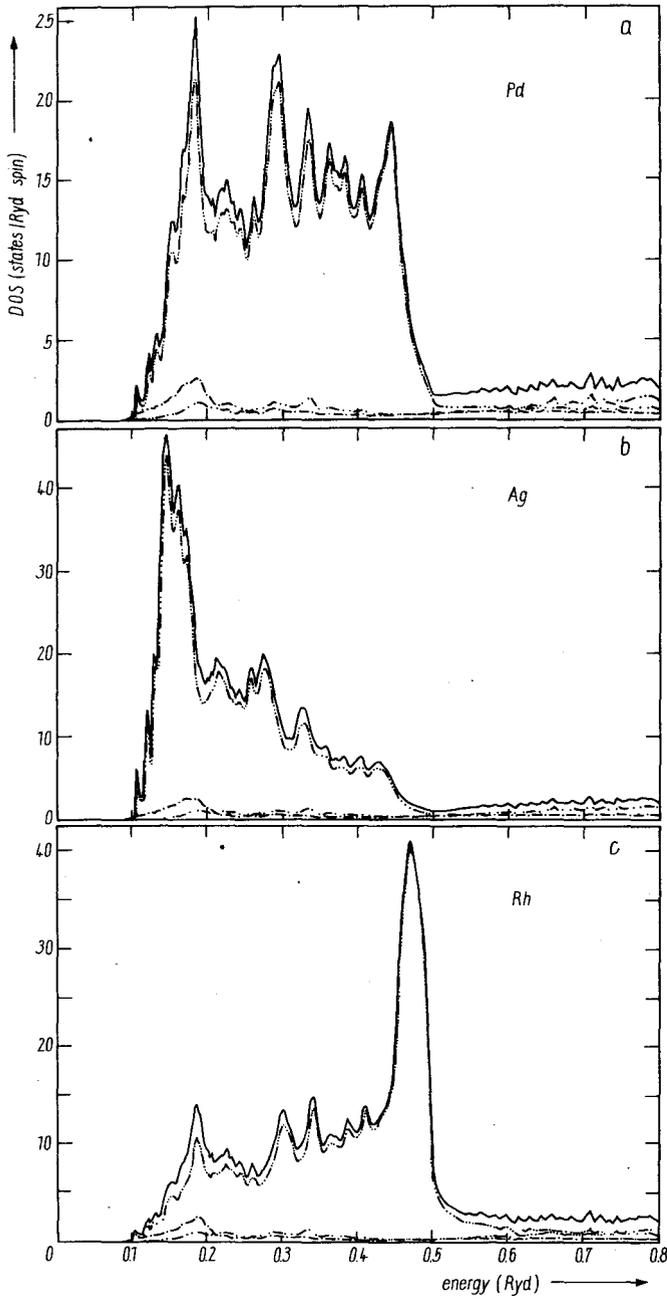


Fig. 1. Partial density of states of a) Pd, b) Ag, and c) Rh; solid line: total partial DOS, dash-dotted lines: angular momentum resolved densities (1 dot: $l = 0$; 2 dots: $l = 1$, 3 dots: $l = 2$)

This alloy was chosen because here experimental susceptibility data for a number of Pd-Rh-Ag alloys are in existence. The alloy possesses the f.c.c. structure and its lattice constant has been estimated from the lattice constants of binary Pd-Ag and Pd-Rh /8, 9/ alloys to be 0.3889 nm. The calculation was carried out non-charge self-consistently using potentials $V^\alpha(\vec{r})$ obtained by the Mattheis construction /10/ from atomic charge densities /11/.

The scattering matrix t_{CPA} was calculated for 217 energy points between 0 and 0.8 Ryd above the muffin-tin zero using (3) and (4). For each energy three to twelve CPA iterations were necessary to reach convergence. Fig. 1a to c show the resulting partial densities of states (DOS) for each component while Fig. 2 gives the total density of states. All energies are given relative to the muffin-tin zero, which is about 0.46 Ryd below the Fermi energy.

The partial DOS of Pd (Fig. 1a) naturally dominates the total DOS (Fig. 2). The prominent peaks covering the whole range of energy between 0.1 and 0.5 Ryd can easily be related to the DOS curve of pure Pd /12/.

In contrast, the partial densities of states of Ag and Rh do not resemble the DOS of the pure metals /12/. The main contribution of Ag (Fig. 1b) occurs

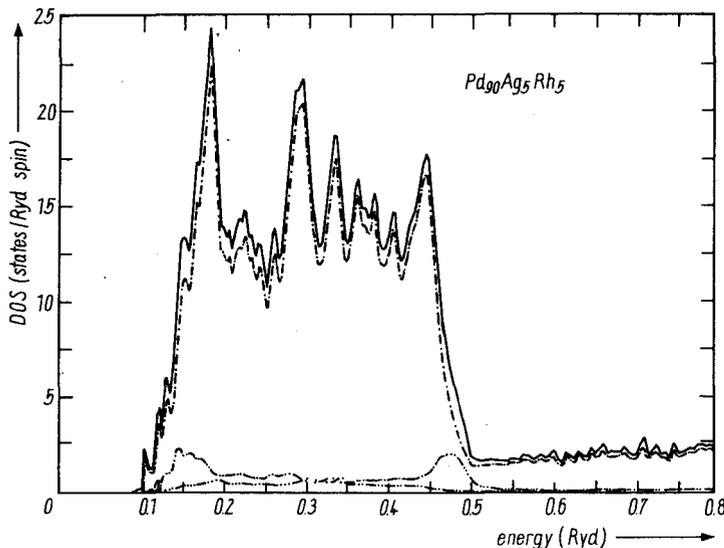


Fig. 2. Density of states of $\text{Pd}_{90}\text{Ag}_5\text{Rh}_5$; solid line: total DOS; dash-dotted lines: partial concentration weighted component densities (1 dot: Pd, 2 dots: Ag, 3 dots: Rh)

as a single sharp peak around 0.16 Ryd, whereas pure Ag shows a number of peaks around the same energy. Between 0.2 Ryd and the Fermi energy is a wide structure which does not occur in pure Ag and which is due to hybridization. Rh presents a sharp peak just above the Fermi energy and a broad structure below whereas pure Rh shows a broad peaky structure over the whole energy range, very similar to that of pure Pd.

Altogether, this example clearly demonstrates that the CPA equations can readily be applied to a ternary alloy system.

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References

- /1/ R. SOVEN, Phys. Rev. 156, 809 (1967).
- /2/ J.S. FAULKNER, Progr. mat. Sci. 27, 1 (1982).
- /3/ G. SCHADLER and P. WEINBERGER, J. Phys. F 16, 27 (1986).
- /4/ W.M. TEMMERMAN and A.J. PINDOR, J. Phys. F 13, 1869 (1983).
- /5/ M.C. MUÑOZ, B.L. GYORFFY, and K. VERHUYCK, J. Phys. F 13, 1847 (1983).
- /6/ H. WINTER and G.M. STOCKS, Phys. Rev. B 27, 882 (1984).
- /7/ A. HAHN and W. TREUTMANN, Z. angew. Phys. 26, 129 (1969).
- /8/ E. RAUB, J. less-common Metals 1, 3 (1959).
- /9/ F. KRÜGER and G. GEHM, Ann. Phys. 16, 191 (1983).
- /10/ L.F. MATTHEIS, Phys. Rev. 133, A1399 (1964).
- /11/ F. HERMAN and S. SKILLMAN, Atomic Structure Calculations, Prentice Hall, New Jersey 1963.
- /12/ V.L. MORUZZI, J.F. JANAK, and A.R. WILLIAMS, Calculated Properties of Metals, Pergamon, New York 1977.

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