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Calculations of Electronic Structure and Properties of Ag–Pd Alloys Using an APW–VCA Method

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Abstract—The electronic density of states, electronic specific heat $\gamma(x)$, and absolute diffusional (differential) thermopower $S(x)$ of disordered Ag_xPd_{1-x} alloys are calculated using the virtual-crystal approximation of Schoen and formalism of augmented plane waves. The results obtained are compared with experimental data and calculations using the coherent-potential approximation.

INTRODUCTION

Among the theoretical models used for calculations of the electronic structure and properties of disordered alloys, the coherent-potential approximation (CPA) [1] is one of the most widely used. The initial CPA model has now been significantly improved by combining it with various methods of band-structure calculations, such as tight-binding (TB), Korringa–Kohn–Rostoker (KKR), linear combination of muffin-tin (LMTO) or atomic (LCAO) orbitals, and other methods. Significant progress was achieved within this approach in calculations of electronic energy spectra, optical properties, and the Fermi surfaces of solid solutions [2–6]. On the other hand, the results of *ab initio* calculations within the CPA scheme of such alloy properties as electronic heat capacity, electrical resistivity, and thermopower do not always agree well with experimental data, especially for alloys with a high concentration of transition metal [2, 3, 7]. Another disadvantage of the CPA approach, (in particular, of its early versions) is the strong dependence of the calculation results on the parameter of scattering δ. This parameter determines the energy interval between the *d* resonances of the alloy components and, as a rule, cannot be chosen unambiguously [2–4].

In this work, the electronic energy structure and some properties of Ag–Pd alloys are calculated using the augmented-plane-wave (APW) method within the virtual-crystal approximation (VCA) of Schoen [8]. Contrary to the better known virtual-crystal model introduced by Parmenter [9], the VCA method proposed by Schoen does not use an averaged one-component potential, thereby allowing one to reveal individual features of the alloy constituents in the spectra. As for mathematical description and computer realization, the VCA method is significantly simpler than the latest CPA versions and does not use adjustable parameters. Recently, we reported the application of this method for calculating the electronic structure of Cu–Ni alloys [10] and demonstrated that the calculated electronic spectra and alloy properties showed nearly the same and, in some cases, even better agreement with experimental data than the results of calculations utilizing the CPA method.

In this work, we present the results of calculations of the electronic energy spectra, electronic specific heat, and diffusional thermopower for disordered Ag–Pd alloys in the whole concentration range. Particular attention is paid to calculations of the absolute thermopower as a function of alloy composition. In most theoretical approaches, calculations of thermopower utilize adjustable parameters or the parameters taken from experimental data [11, 12]. *Ab initio* calculations agree fairly well with the experimental data only in the case of small impurity concentrations, where Matthiessen's rule is fulfilled and the Fermi surface of the host metal remains almost unchanged [13]; for higher concentrations, no agreement between calculated and experimental data is attained. The most significant progress in calculations of thermopower was achieved by Butler and Stocks [7] who used the KKR–CPA scheme for Ag_xPd_{1-x} alloys with $x = 0.2$–0.8.

We have chosen silver–palladium alloys for the present calculations for several reasons. First, an almost complete set of experimental data is available for these alloys (and also for the copper–nickel system). Second, this system is very popular for checking various theoretical models, from the rigid-band model to the coherent-potential approximation. Finally, Ag–Pd alloys are the only system for which *ab initio* calculations of the absolute thermopower as a function of composition have been performed in a wide range of concentrations. Thus, a quantitative comparison with the results obtained using different calculational techniques is possible.

CALCULATIONAL PROCEDURE

In this work, the electronic energy spectra were calculated using the APW method within the virtual-crystal approximation (APW–VCA) [8]. The APW–VCA method was developed by Schoen for disordered solid solutions and nonstoichiometric compounds and was then successfully used by many others to calculate the electronic structure and properties of nonstoichiometric compounds. We have recently employed this method for metallic solid solutions, in particular, for Cu–Ni alloys [10]. Because of the tedious calculations necessary in the traditional APW scheme, the potential used in this work (as well as in the earlier study [10]) is not self-consistent. For this reason, of particular importance are the choice of initial approximation and comparison of the results obtained for pure constituent metals with the available experimental data and the results of self-consistent calculations. The crystal muffin-tin (MT) potential with separated Coulomb and exchange parts was constructed using the Mattheiss method. The self-consistent Roothaan–Hartree–Fock atomic wave functions [14], which have a convenient analytic representation

$$\Phi_{nlm} = \sum C_{nlp}\chi_{plm}(r, \theta, \varphi),$$

were used as the initial approximation for the MT potential. Here,

$$\chi_{plm}(r, \theta, \varphi) = D_{lp}(r)Y_{lm}(\theta, \varphi) \qquad (1)$$

and

$$D_{lp}(r) = \frac{1}{\sqrt{2N_{lp}!}}(2Z_{lp})^{N_{lp}+1/2}r^{N_{lp}-1}e^{-Z_{lp}r}.$$

The parameters r, θ, and φ are spherical coordinates; N_{lp} is the number of the electronic shell; the coefficients C_{nlp} and Z_{lp} for pure constituent metals are determined in [14], and here we assume that they are linear functions of composition. The Coulomb part of the potential had the form

$$V_c(\mathbf{r}) = V_k(\mathbf{r}) + \sum_t n_t \sum_\eta c_{\eta t} V_\eta(R_t, \mathbf{r}), \qquad (2)$$

where $V_k(\mathbf{r})$ is the Coulomb potential of a given (central) atom of type k, $V_\eta(R_t, \mathbf{r})$ is the contribution to the Coulomb potential from an atom of type η in the tth atomic shell of radius R_t, n_t is the coordination number of the tth coordination shell, and $c_{\eta t}$ is the partial [(in the tth shell)] atomic concentration of atoms of type η.

The exchange potential was constructed using the Slater approximation with the correction factor α for the exchange and correlation effects

$$V_x(\mathbf{r}) = \alpha V_x^S(\mathbf{r}), \qquad (3)$$

where

$$V_x^S(\mathbf{r}) = -6\left\{\frac{3}{8\pi}\left[\rho_k(\mathbf{r}) + \sum_t n_t \sum_{\eta=1}^{2} c_{\eta t}\rho_\eta(R_t, \mathbf{r})\right]\right\}^{1/3}.$$

Here $\rho_k(\mathbf{r})$ is the electron density of the central atom and $\rho_\eta(R_t, \mathbf{r})$ is the contribution to the electron density from an atom of type η in the tth coordination shell. The exchange correction factors α for pure metals satisfy the virial theorem and are 0.70114 and 0.70128 for silver and palladium, respectively [15]. In alloys, the parameter α and the lattice parameter a are assumed to be linear functions of the composition

$$a = xa_{\mathrm{Ag}} + (1-x)a_{\mathrm{Pd}},$$

where a_{Ag} and a_{Pd} are the lattice parameters of Ag and Pd, and x is the concentration of Ag in the alloy.

The Schrödinger equation was solved using a standard procedure for the APW method [16]. The details of the procedure, including the form of the matrix elements of the secular determinant, can be found in [10].

Calculated and experimental data for some typical energy intervals (in Ry) in silver and palladium

Intervals	Ag			Pd		
	[18]	this work	experimental data*	[17]	this work	experimental data
Γ_{12}–$\Gamma_{25'}$	0.069	0.068	0.080	0.103	0.114	–
X_5–X_2	0.020	0.017	0.022	0.091	0.051	–
X_5–X_3	0.244	0.221	0.228	0.365	0.390	0.37 [24]
X_5–X_1	0.256	0.231	0.250	0.396	0.402	–
$L_{3(2)}$–$L_{3(1)}$	0.120	0.124	0.134	–	–	–
$L_{3(2)}$–L_1	0.220	0.191	0.216	0.336	0.352	–
X_4–X_5	0.385	0.503	–	0.308	0.308	–

* Most experimental data are taken from the work of Fuster *et al.* [23] where the original references can be found.

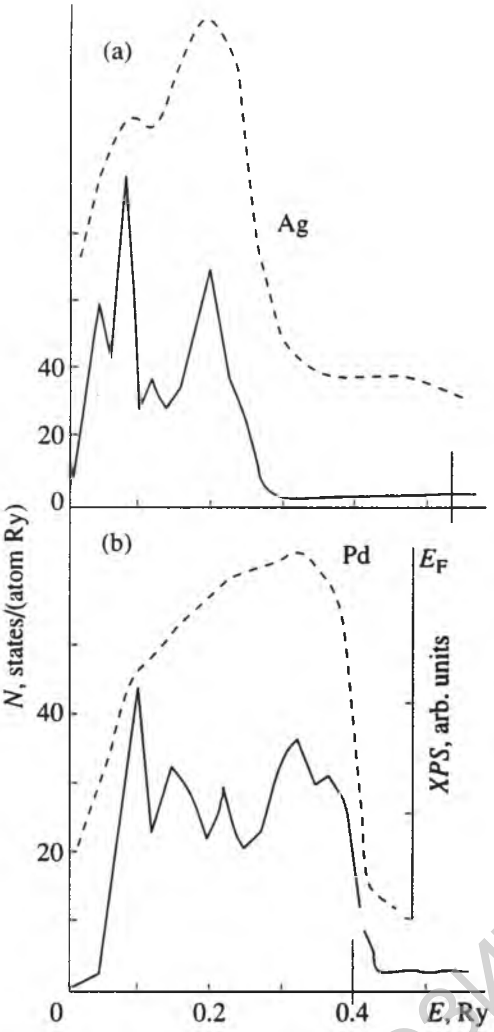

Fig. 1. Calculated (solid lines) electron density of states in (a) silver and (b) palladium in comparison with their XPS spectra (dashed lines).

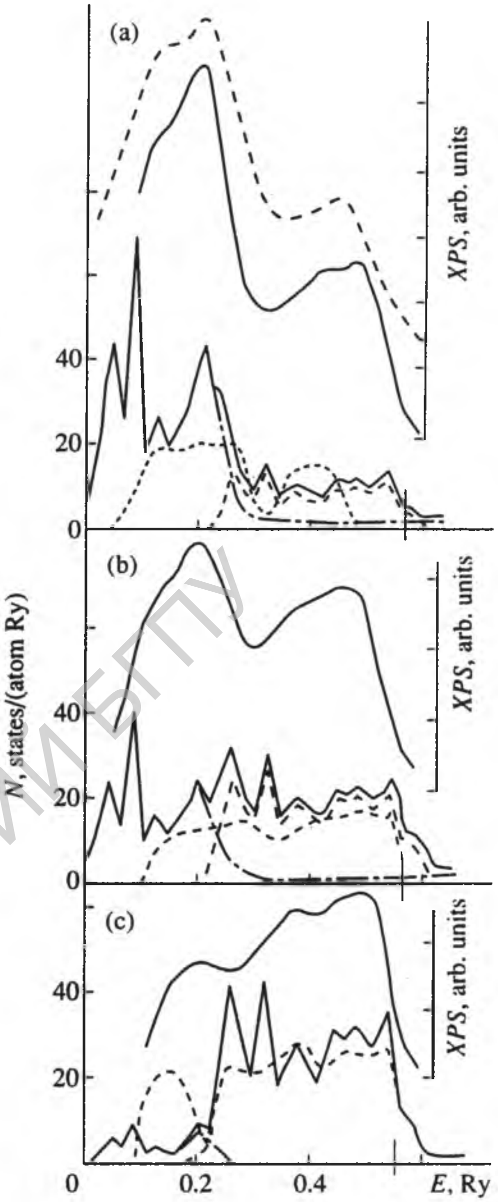

Fig. 2. Calculated total (solid lines) and partial (dashed lines for Pd and dash-dotted lines for Ag) electronic densities of states in Ag_xPd_{1-x} alloys with x = (a) 0.7, (b) 0.4, and (c) 0.1 in comparison with the published XPS spectra [19, 20] and the results of calculations (short dashes) using TB–CPA (x = 0.7 and 0.4) [3] and KKR–CPA (x = 0.2, see Fig. 2c) [5] schemes; the XPS spectra presented in Fig. 2a are related to the x = 0.71 (dashed line) [20] and x = 0.65 (solid line) [19] compositions.

To calculate the density of states (DOS), integration over the Brillouin zone was carried out using the method of tetrahedra.

RESULTS AND DISCUSSION

We used the $4d^{10}5s^1$ configuration for Ag and $4d^95s^1$ for Pd. The lattice parameters and the radii of the MT spheres were taken to be $a = 7.7316$ au, $R_{MT} = 2.7335$ au for Ag and $a = 7.3355$ au, $R_{MT} = 2.5935$ au. for Pd. The initial approximation [for MT potentials] used in this work was first tested in calculations of the electronic structure of the pure metals. The characteristic energy intervals for silver and palladium are presented in the table. It follows from this table that our results agree fairly well with the existing experimental data and the results of earlier self-consistent calculations using an APW method for palladium [17] and an LAPW method for silver [18]. Figure 1 shows the calculated electronic DOS's for Ag and Pd in comparison with the experimental X-ray photoelectron spectra (XPS) [19]. The calculated and experimental spectra are matched in energy (both in the scale and positions of the Fermi level). It is clearly seen that the *d* peaks in the two spectra correspond well to one another with regard to their relative positions and their positions with respect to the Fermi level. For example, according to the XPS data, the right-hand *d* maximum in silver is 4.8 eV or 0.35 Ry below the Fermi level, which should be compared with the calculated value of 0.34 Ry. The the calculated spacing between the *d* peaks (0.12 Ry) agrees well with the result of the XPS measurements (0.11 Ry), whereas the agreement between the calculated and measured half widths of the *d* band is worse: 0.20 and 0.26 Ry, respectively. For palladium, both calculated and measured half widths of the *d* band and the peak positions correspond well to each other: the calculated half width for Pd is 0.34 Ry. and the measured one is 4.8 eV or 0.35 Ry [19, 20].

In the Ag–Pd system, the energy spectra were calculated for nine alloy compositions covering the whole range of concentrations with an interval of 10 at. %. Figure 2 shows the calculated DOS's for alloys with 30, 60, and 90 at. % Pd. The solid curves are the total DOS's $N(E)$, and the partial DOS's, $N_{Pd}(E)$ and $N_{Ag}(E)$, are plotted as dashed and dash-dotted lines, respectively. The position of the Fermi level is marked with a vertical bar. Also shown in Fig. 2 are the experimental data evaluated from XPS and ESCA spectra, and the results of TB–CPA [3] and KKR–CPA [5] calculations (short dashes). The energy scales of the DOS curves are matched to have the same Fermi energy. The main features in the experimental DOS curves and the positions of the *d* peaks with respect to the Fermi level derived from the XPS data correlate fairly well with the results of calculations. As the palladium concentration is increased, the intensity of the corresponding *d* peak increases, while its position is almost independent of composition. For example, according to the XPS data, this additional peak in Ag-rich alloys is observed 2.0–2.1 eV (0.15 Ry) below the Fermi level. This quantity should be compared with the calculated value of 0.16 Ry. A comparison of our results with those obtained using the CPA method (short-dashed lines in Figs. 2a–2c) shows that the DOS's calculated using the CPA method (in particular the KKR–CPA calculations by Pindor *et al.* [5], see Fig. 2c) agree better with the experimental data on the subband widths. whereas the relative intensities of the components are better reproduced in our calculations.

The numerical values of the density of states at the Fermi level $N(E_F)$ were used for calculating the electronic specific heat coefficient γ via the relation

$$\gamma = \frac{\pi^2 k_B^2}{3} N(E_F)(1+\lambda), \qquad (4)$$

where λ is the electron–phonon coupling constant, which was assumed to vary linearly with composition between the empirical values of 0.1 and 0.7 [15] for Ag and Pd, respectively. Figure 3 shows the calculated compositional dependence $\gamma(x)$ (filled circles + solid line) in comparison with the experimental data [21] (open circles + dashed line) and the results of the latest calculations by Laufer and Papaconstantopoulos [6] (semifilled circles), who used the TB–CPA method. It follows from such a comparison that our results agree fairly well with the experimental data. For alloys with more than 50 at. % Ag, this correspondence is as good as that obtained using the CPA method, while for palladium-rich alloys with less than 20 at. % Ag, our results better reflect the experimentally observed changes in γ with composition.

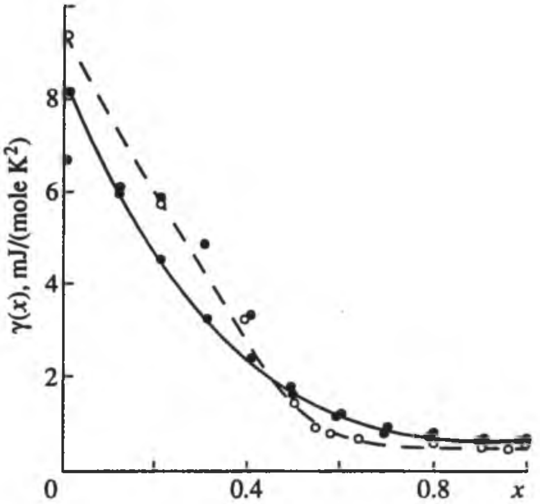

Fig. 3. The electronic specific heat coefficient as a function of concentration in Ag_xPd_{1-x} alloys: our calculations (filled circles) in comparison with experimental data [21] (open circles) and the results of calculations using a TB–CPA method [6] (semi-filled circles).

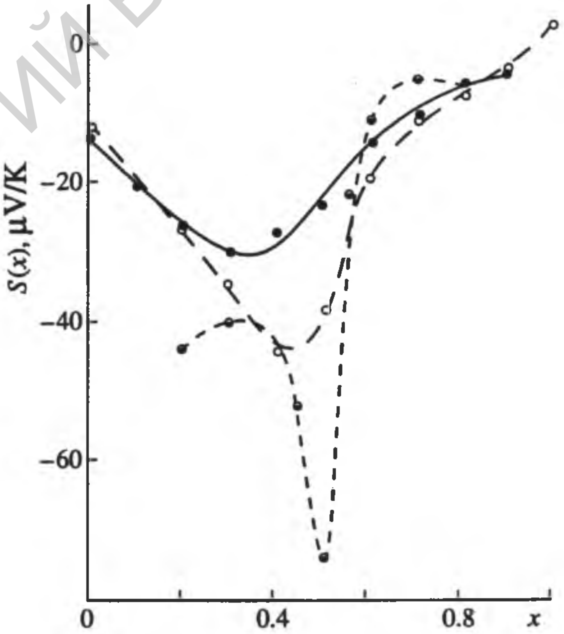

Fig. 4. The absolute differential thermopower at 100°C as a function of concentration in Ag_xPd_{1-x} alloys: our calculations (filled circles) in comparison with experimental data [22] (open circles) and the results of calculations using a KKR–CPA method [7] (semi-filled circles).

Earlier [10], we showed that the absolute diffusional (differential) thermopower of transition-metal alloys with noble metals is given by

$$S = \frac{\pi^2 k_B^2 T}{3|e|} \frac{1}{N(\varepsilon_F)} \left(\frac{dN}{d\varepsilon}\right)_{\varepsilon_F}. \quad (5)$$

which is a rather good approximation, even starting from dilute (several percent transition-metal impurity) alloys. Here, k_B is Boltzmann constant, e is the electron charge, and $N = N_s + N_d$ is the total DOS in the s and d bands. The derivative $(dN/d\varepsilon)_{\varepsilon_F}$ was calculated by approximating the DOS $N(\varepsilon)$ near ε_F with a parabola. The energy interval for approximation was successively decreased until the left-hand and right-hand derivatives at ε_F had become equal to the fifth decimal place. Figure 4 shows the calculated absolute thermopower S at 100°C (solid line) in comparison with the experimental data for Ag–Pd alloys [22] (dashed line) and the results of self-consistent calculations within the KKR–CPA scheme [7] (these results are corrected to correspond to the same temperature). Apparently, our results correspond better to the experimental data, in particular for Pd-rich compositions.

CONCLUSION

Thus, we have demonstrated that, even without a self-consistent potential (but with a good initial approximation), the APW–VCA scheme of Schoen may give a satisfactory description of the electronic density of states in disordered alloys, showing the main trends in its changes with composition. The densities of states at the Fermi level thus obtained were then used to calculate such properties as the electronic heat capacity and diffusional thermopower. Satisfactory agreement with the experimental data was obtained in the whole range of concentrations and, for Pd-rich alloys, the agreement was even better than in the case of calculations that employed the CPA method.

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