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Photoemission study of the electronic structure of silver palladium alloys

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Abstract. Photoemission experiments have been made on a series of AgPd alloys including the pure components. In Ag-rich alloys the d levels of the Pd atoms occupy a resonant bound state which has a width ~ 1 eV at infinite dilution increasing to ~ 1.7 eV at 30% Pd. It is argued that a major contribution to this breadth at infinite dilution is the spin orbit splitting of the d levels; the resonance broadening, 2Δ on the Anderson model, being estimated as 0.5 eV. The increase in breadth with increasing Pd content is attributed to interatomic d-d broadening between Pd atoms. The isolated impurity atom is believed to possess ~ 0.38 d holes and contribute to the density of states at the Fermi level an amount ~ 0.185 eV⁻¹ per atom. These values are compatible with other properties of AgPd alloys namely the electron specific heat and residual electrical resistance. Comparison is made with the analogous CuNi alloys.

Above 40% Pd the d electrons occupy true band states and it is suggested that the transition from the resonant bound state to the band state is sharp and may be characterized as a semiconductor-metal transition for the Pd d electrons.

The experimental data clearly show the effects of structural disorder on the sharp band structures of the pure components. In the case of PdAg alloys the blurring of the band structure due to disorder and the transference of electrons from Ag conduction to Pd d states on account of the weak screening of the Ag impurity atoms account for the rapid decrease in electron heat and paramagnetic susceptibility of Pd due to alloying with Ag.

Direct transitions between conduction band states, Λ_1 - Λ_1 transitions, were observed in pure Ag and the Ag_{0.95}Pd_{0.05} alloy.

1. Introduction

1.1. Choice of system

Although there is much experimental data regarding the properties of alloys, it is nevertheless the case that a detailed understanding of these properties is not available. Apart from Pb, the so-called nearly free electron metals are very poor solvents and unsuitable for alloying studies. The noble metals on the other hand form extensive solid solutions with both polyvalent and many transition metals. In the former case the properties of the alloys are determined by the changes in the conduction electron gas and these are in general small and their subtlety such that present understanding is limited to very general conclusions of the form 'the transport properties are not incompatible with rigid band behaviour', Ziman (1961). Alloys of noble metals with a transition metal however often show radical changes of behaviour which may be associated with the presence of impurity d states: the Kondo phenomenon is a particularly striking example. Completely miscible systems like AgPd, AuPt, CuNi show pronounced but regular variations over the whole range of compositions. So simple in fact is the change in behaviour that conflicting models, such as the rigid band model (Mott 1936), the virtual crystal model (Lee and Lewis 1969) and the minimum polarity model (Kirkpatrick *et al.* 1969) have been reasonably successful in interpreting experimental data.

In the case of the dilute alloy where a small amount of transition metal is dissolved in

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say Cu the theoretical work of Friedel (1958) and Anderson (1961) has been particularly successful in describing the magnetic, thermal and transport properties. Optical measurements of AuPd (Abeles 1966) and AgPd (Myers *et al.* 1968) have provided direct evidence for the existence of the resonant bound state in these alloys. In addition it was shown that the d states undergo little or no movement in energy on alloying, indicating that they are dependent on the local potential rather than the average potential, as would be the case for the rigid band or virtual crystal models. Confirmation of these results has been provided by photoemission measurements on CuNi (Seib and Spicer 1968), AgPd (Norris and Nilsson 1968) and AgMn (Walldén 1970). Photoemission has the advantage that, in contrast to ordinary optical studies, it gives more direct information about the density of occupied states in the alloy. In this report we describe photoemission measurements made on a series of AgPd alloys. The object has been to follow in detail the density of electron states with particular attention to the width of resonant levels, d band structure, the height at the Fermi level and the variation of these quantities with composition. The AgPd alloy system was chosen on account of the complete miscibility and because the Ag and Pd 4d electrons are clearly separated in energy; furthermore it is very well documented in terms of other physical properties.

1.2. The photoemission process

The photoemission process is not fully understood. The usual approximation is to assume three stages:

- (a) photoexcitation
- (b) travel to the metal/vacuum interface
- (c) escape

In the past there has been considerable discussion (Berglund and Spicer 1964a) as to whether the one electron wave vector $\mathbf{k}$ is conserved in the optical transition. In the case of direct transitions the energy distribution of photoemitted electrons immediately after excitation is, assuming constant matrix elements,

$$P(\epsilon, \hbar\omega) = \int d^3k \delta(\epsilon_f - \epsilon_i - \hbar\omega) \cdot \gamma(\epsilon - \epsilon_f)$$

ϵ being the energy of the excited electron relative to the Fermi level and i and f referring to initial and final states. The resulting photoemission spectrum is thus a rather complicated quantity depending upon the location of states in $\mathbf{k}$ space as well as their energies. Such is the case for pure metals, (Nilsson *et al.* 1969, Smith 1969). In the case of our present interest, photoemission from a randomly disordered alloy, the theoretical justification for direct transitions that all states are described by Bloch waves for which $\mathbf{k}$ is a good quantum number, is greatly weakened. If $\mathbf{k}$ is not important, the spectrum reduces to the well known expression for the so called non-direct transitions

$$P(\epsilon, \hbar\omega) = B N_i(\epsilon - \hbar\omega) N_f(\epsilon)$$

where $N_i(\epsilon - \hbar\omega)$ and $N_f(\epsilon)$ refer to the densities of the initial and final states respectively. In general only features corresponding to variations in $N_i(\epsilon - \hbar\omega)$ are observed. The non-appearance of any structure associated with the final density of states is probably due to the fact that inelastic scattering of the photoexcited electrons tends to preferentially weaken such structure, and that in general $N_f(\epsilon)$ is a much smoother function of energy than $N_i(\epsilon - \hbar\omega)$.

2. Experimental technique

Measurements were made on bulk samples and evaporated films with incident radiation energies in the interval 4–11 eV obtained from a hydrogen discharge lamp and a McPherson ultraviolet monochromator. The measuring chamber with working pressure $< 10^{-9}$ torr was isolated from the relatively high pressure in the monochromator by a LiF window.

The energies of photoemitted electrons were analyzed using a cylindrical collector carrying a modulated retarding voltage relative to the sample.

All measurements on alloys were made with bulk samples. Usually it is preferable to work with evaporated films but this was not practicable in the case of Pd alloys due to reactions with filament materials. Samples measured $20 \times 10 \times 2$ mm and were prepared by melting weighed amounts of the components by induction heating in sealed quartz tubes. The alloys were annealed for a week at 900°C to ensure homogeneity. They were then rolled, cut to shape and mechanically polished. No electropolishing was used. To obtain sharp electron energy distribution curves it was necessary to clean samples *in vacuo* prior to measurements. This was arranged by heating the sample to 500°C , bombarding the surface with argon ions and thereafter reannealing to remove surface damage. During ion bombardment the accelerating potential was 400 volts and the ion current 4 mA. It was found that one such cleaning cycle was sufficient to produce sharp distribution curves; prolonged bombardment on the other hand tended to destroy the surface. Microprobe analysis showed the samples to be within 0.7% of the nominal concentrations. In certain cases the work function of the sample was reduced by depositing a thin layer of caesium onto the surface; the Cs vapour was obtained within the chamber by electrically heating a mixture of caesium chromate and silicon powder in a nickel tube.

3. Results

The electron energy distribution curves obtained in these experiments are described in the figures 1 to 7, with the exception of figure 5, the curves are plotted against a reduced energy $E_k + e\phi - \hbar\omega$ where E_k is the kinetic energy of the photoemitted electron, ϕ the work function of the sample and ω the angular frequency of the incident light. On this scale zero corresponds to the Fermi level.

3.1. *d* states

Figure 1 shows electron energy distribution curves obtained from bulk silver and two silver palladium alloys for an incident photon energy of 10.2 eV. The result for Ag agrees with earlier measurements (Krolikowski 1967) on an evaporated film; the high peaked structure lying below -3.5 eV corresponds to transitions from 4d states and the flatter band extending up to the Fermi edge to transitions from the 5s p conduction band states.

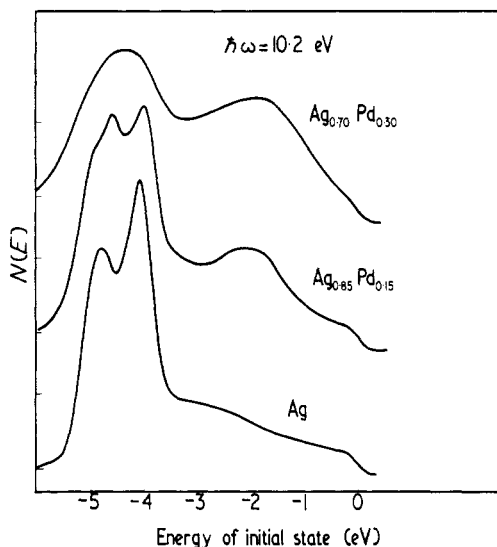


Figure 1. Photoemission spectra obtained with bulk samples of silver and two silver palladium alloys using incident radiation of 10.2 eV photon energy.

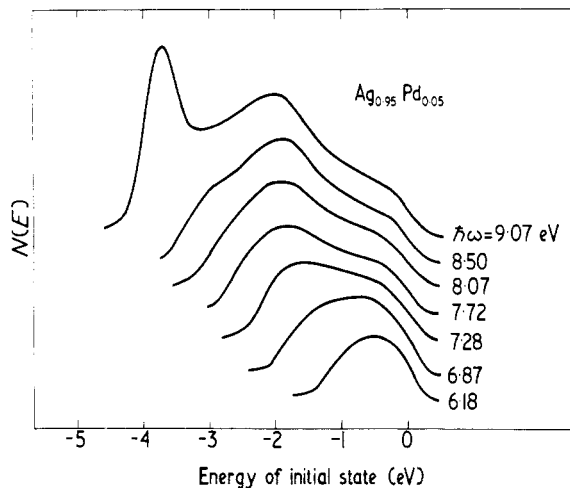


Figure 2. Photoemission spectra obtained with different photon energies for an alloy containing 5 at. % Pd.

The data for the 15% Pd alloy shows an extra hump at approximately -2.1 eV. Curves obtained from a 5% Pd alloy with different photon energies are shown in figure 2; the extra hump is again clearly discernible at the same energy, furthermore on changing the photon energy it does not move relative to the Fermi edge indicative of non-direct transitions from initially occupied electron states. Anticipating later discussion we attribute the hump to the 4d levels of the Pd, a conclusion in agreement with earlier optical measure-

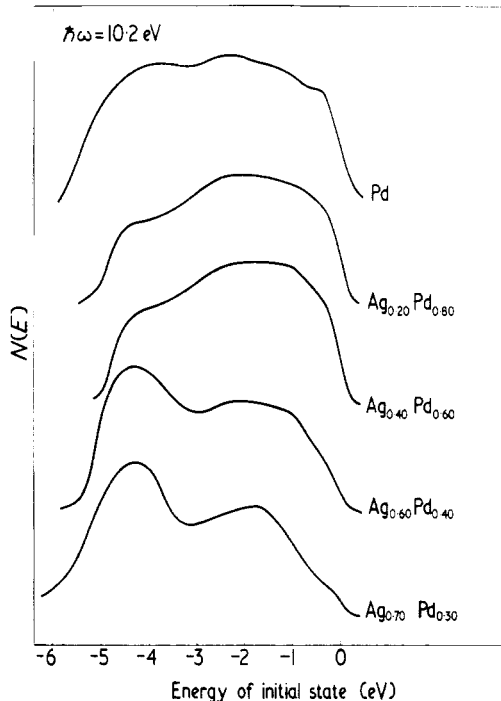


Figure 3. Energy distribution curves obtained with $\hbar\omega = 10.2$ eV from alloys containing between 30 and 100 at. % Pd, illustrating the development of the Pd d states from a localized level to a true band.

ments on AgPd alloys (Myers *et al.* 1968). Regarding the breadth of the Pd levels, even after allowing for experimental broadening, we estimate the half value width for a 5% Pd alloy to be 1.0 eV. On increasing the Pd concentration to 30%, figure 1, the Pd 4d level increases in strength relative to the Ag 4d band and broadens; this process continues through to pure Pd (see figure 3). Because of the rather low photon energies used in these experiments it is not possible to discern the low energy limit of the d states. It is clear however that the Pd 4d levels broaden from a relatively narrow component at low Pd concentration with half value width ~ 1 eV to a band more than 4 eV wide for Pd-rich alloys.

The magnitude of the density of states at the Fermi level is indicated by the relative height of the shoulder immediately below the Fermi edge. Up to 30% Pd the shoulder is quite small compared with other structure whereas for 60% Pd and above a considerable increase is observed, figure 3. Comparing the data for the $\text{Ag}_{0.70}\text{Pd}_{0.30}$ and $\text{Ag}_{0.60}\text{Pd}_{0.40}$ samples, a noticeable flattening of the Pd 4d level between -1.0 and -2.4 eV can be seen for the latter composition. This flattening is also evident in the curves for alloys of higher Pd concentration; in pure Pd distinct structure is resolved.

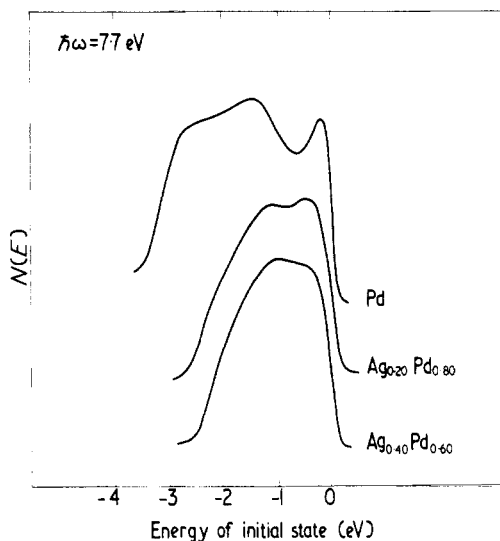


Figure 4. Energy distribution curves for pure Pd and two AgPd alloys showing the effect of alloying on the high energy peak in the Pd 4d band.

A consequence of introducing impurities, whether they be Pd or Ag, into the lattice of the pure metal is to cause a general blurring of the spectrum. This may be seen in figure 1 on comparing the relative strength of the peak at the high energy end of the d band structure in pure Ag and the 15% Pd alloy. For the 30% Pd alloy no structure at all can be seen. Figure 4 shows energy distribution curves for pure Pd and two alloys taken with photons of energy 7.7 eV. The weakening of the high energy peak in the neighbourhood of the Fermi edge is again clearly evident. On the other hand alloying causes little movement in the position of the d band edge of Ag as can be seen by comparing the data for pure Ag and $\text{Ag}_{0.85}\text{Pd}_{0.15}$; this is in agreement with earlier optical work on these alloys. The structure associated with the Pd d band also remains at constant position with increasing Ag content. Some displacement of the high energy peak is apparent, figure 4, but it is difficult to decide whether this reflects a genuine movement of the energy levels or whether it is a consequence of the proximity to the Fermi edge coupled with the fact that it weakens as Ag is dissolved into Pd.

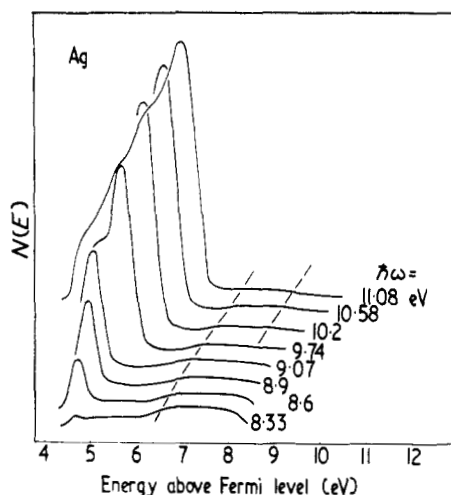


Figure 5. Energy distribution curves obtained from an evaporated film of Ag. The broken lines indicate the position of two shoulders associated with direct transitions between conduction band states.

3.2. Conduction band states

In figure 5 are shown results obtained from an Ag film evaporated onto a glass substrate. The curves are noticeably sharp with structure in the d band region even for the highest photon energies and there is little evidence of scattered electrons. Immediately below the d band edge the curves are rather shallow in contrast to the results from the bulk sample shown in figure 1 and observed in other measurements. In this region there is a shoulder facing towards lower energy which moves away from the Fermi edge as the photon energy

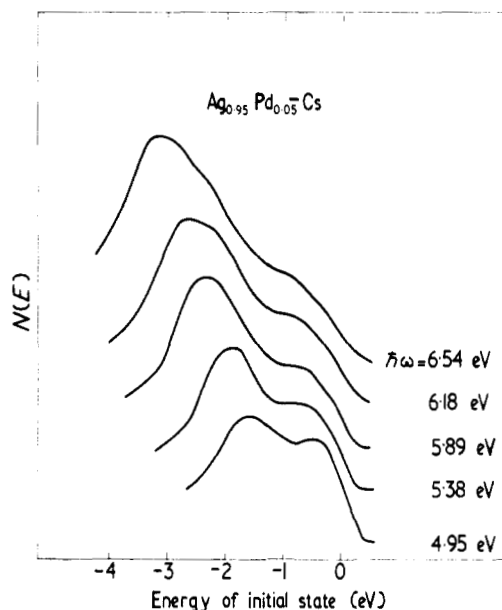


Figure 6. Energy distribution curves obtained with a caesiated 5 at.% Pd alloy. The shoulder corresponding to the low energy limit of direct transitions between conduction band states can be seen as the feature which moves from -0.5 eV ($\hbar\omega = 4.95$ eV) to -0.9 eV ($\hbar\omega = 6.54$ eV) as the photon energy is increased.

is increased. This characteristic will be attributed later to direct transitions between Λ_1 states. For $\hbar\omega > 9.7$ eV a weak second shoulder, which moves in correspondence with the first, can be observed. No alloy sample with normal work function showed these effects. However, by using lower photon energies and a 5% Pd sample, the work function of which had been decreased by depositing a very thin layer of Cs onto the surface, it was possible to observe the $\Lambda_1 - \Lambda_1$ feature (figure 6). Figure 7 shows two curves obtained with $\hbar\omega = 6.18$ eV from caesiated samples of Ag and the 5% Pd alloy. Both results were obtained in the same vacuum, without opening the chamber, by evaporating the Ag onto the alloy surface immediately after the measurements on the latter were completed. It can be seen that the $\Lambda_1 - \Lambda_1$ transition has moved slightly to higher energies and weakened. This movement occurred in all results where the transition could be observed and was an average 0.2 eV. A measurement made on a caesiated 15% Pd alloy showed no conduction band structure.

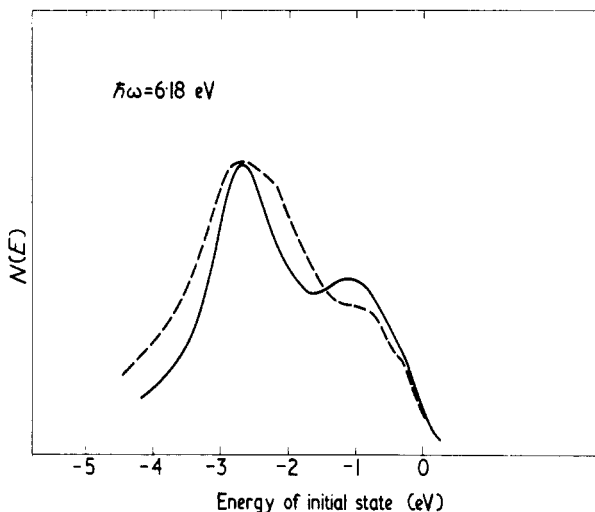


Figure 7. Photoemission curves obtained with a caesiated 5 at. % Pd alloy and a caesiated Ag film for $\hbar\omega = 6.18$ eV. The $\Lambda_1 - \Lambda_1$ feature in the alloy curve (-0.8 eV) is weaker and lies at slightly higher energy compared with the result obtained with pure Ag. Full curve, Ag-Cs; broken curve, $\text{Ag}_{0.95}\text{Pd}_{0.05}$ -Cs.

4. Discussion

The physical properties of AgPd alloys have attracted much attention of which we mention only the work of Montgomery *et al.* (1967) on the specific heat, Coles and Taylor (1962) electrical resistance and Hoare *et al.* (1953) magnetic susceptibility. Discussion of these properties has been primarily based on Mott's (1936) proposal for the band structure of these alloys, or the proposal as modified by Dugdale and Guénault (1966). Whether one has considered the d electrons of Ag and Pd to occupy a common d band or two separate d bands the essence of all interpretation has been the hypothesis that for alloys containing less than 40% Pd there are no holes in the d states. The data presented in the previous section of this paper will be used to demonstrate that holes are to be associated with Pd atoms at all concentrations of AgPd alloys. Whether there is a proportionately large or small hole content per Pd atom is not important the significant quantity being the density of Pd 4d states at the Fermi level. We shall show that under different circumstances the same hole content per Pd atom can be associated with state densities differing by a factor of 10 or more. However, before taking up the problem of d states we first discuss the data regarding conduction band states.

4.1. Conduction band states

The photoemission data for clean silver, figure 5, are remarkable in that they reveal no structure corresponding to a peak in the final density of states near 6.7 eV above the Fermi level, as has been reported by Krolkowski (1967). Rather, in the region between the d band and the Fermi edge, two shoulders are found which move to lower initial energy as the photon energy is increased. The low energy and stronger shoulder, observed previously by Berglund and Spicer (1964b) with caesiated films, is readily associated with the low energy limit of direct transitions between the first and second conduction bands, that is between Λ_1 states lying along the Γ -L axis in the Brillouin zone. This assignment is consistent with figure 8 where good agreement is found between the position of the shoulder and a curve deduced from Christensen's (1969) band scheme. Features equivalent to the low energy shoulder have been reported for both Cu and Au but it is only with Au that a high energy edge in the conduction band structure has been observed. (Nilsson *et al.* 1970.)

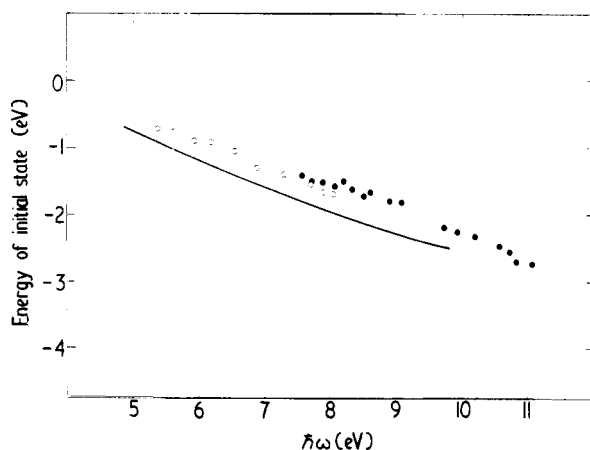


Figure 8. The energy of the initial state as a function of photon energy for direct transitions between Λ_1 conduction band states in Ag. The full curve was obtained from a calculated band scheme (Christensen 1969) whereas the circles correspond to the position of the low energy shoulder in the spectra from Ag films. $\circ$ Ag-Cs; $\bullet$ Ag.

If this correspondence is correct the high energy shoulder in Ag is to be associated with direct transitions from states lying between the Γ point and the square face of the Brillouin zone. The fact that the conduction band structure is seen only with the most dilute alloy, and in much weakened form, is consistent with the presence of disorder favouring non-direct at the expense of direct transitions. As figure 7 shows, the addition of 5% Pd to Ag causes a shift of about 0.2 eV of the Λ_1 - Λ_1 shoulder implying that the conduction states are, as one would suspect, more sensitive to alloying than the d states. The shift to higher kinetic energies could be the result of an upward shift of a common conduction band to allow for the decrease in the electron content and lower atomic number of Pd, or a consequence of a change in the relative positions of the conduction bands in the neighbourhood of the L point. The conduction band states at L_1 and L'_2 are purely s-like and p-like respectively. Cohen and Heine (1958) have pointed out that their separation should be sensitive to the value of the s-p excitation energy in the pure atom, Δ_{sp} . However, according to the published term tables (Moore 1958) Δ_{sp} for Pd, 3.65 eV, is very close to that of Ag, 3.73 eV; consequently little change in the conduction band structure should arise on this account. For little or no distortion, the rigid band shift corresponding to the reduced conduction electron density around each Pd atom may be estimated by assuming a simple parabolic form and the value 7.23 eV for the band breadth in Ag, Christensen *loc cit.*

Then, if, as we shall later show, 0.38 conduction electrons are associated with each Pd atom, the expected movement is 0.15 eV which compares well with the measured shift namely 0.2 eV.

4.2. *d* states

4.2.1. *Ag-rich alloys.* The hump in the photoelectron energy distribution curves at -2.1 eV arising when Pd is added to Ag can only be associated with the presence of Pd. We expect the *d* levels in Pd to lie above those of Ag and the theoretical work of Friedel (1958) and Anderson (1961) provides a good physical picture of their being in spin degenerate resonant bound states. The data of figure 1, as do the earlier optical results, show that the *d* levels of Ag and Pd in Ag rich alloys are well separated and there can be no question of their forming a common *d* band. No appreciable movement of the Ag and Pd *d* states occurs with increasing Pd concentration and any change in the density of states at the Fermi level can only arise through the broadening of the Pd resonant *d* level and its overlap with the Fermi level. The above precludes any application of the rigid band or virtual crystal models.

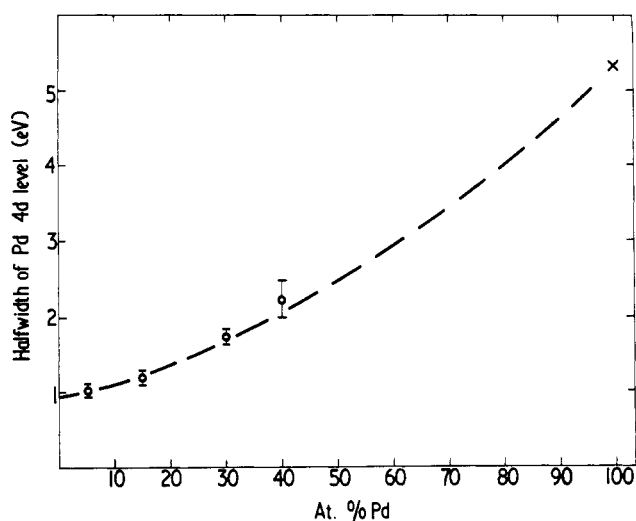


Figure 9. The halfwidth of the Pd 4d level as a function of concentration. The circles represent values obtained from the photoemission data, the cross corresponds to the width of the 4d band at the X point in the energy band diagram calculated by Krogh-Andersen (1969).

Recent discussions of disordered alloys have centred on the coherent potential approximation based on a multiple scattering description Velicky *et al.* (1968) and Soven (1969). This approach correctly predicts the general features observed for the AgPd system that is separate systems of levels corresponding to the *d* states of the constituents which merge together as the impurity concentration is increased. However, so far, only uniform single bands have been considered without the complication of *s-d* hybridization. The width of the impurity band was predicted to increase as the square root of the concentration. In figure 9 are plotted the half value widths of the Pd 4d levels as deduced from our photoemission data. The experimental broadening has been allowed for by the approximate relation

$$(\text{true half width})^2 = (\text{measured half width})^2 - (\text{experimental half width})^2$$

which is strictly true only for Gaussians. Only data up to 40% Pd concentration are

plotted since for higher concentrations the Pd 4d level overlaps that of Ag and cannot be clearly distinguished. The large error bar at 40% reflects this fact. In contrast to the prediction of the coherent potential model the results do not show the square root dependence on concentration. It is unlikely that this difference is due to s-d resonance which contributes primarily to the width at infinite dilution, rather it probably reflects the fact pointed out by Velicky *et al.* (1968) that by treating each site as occupied by an effective atom with some impurity character the coherent potential approximation overestimates the width due to d-d overlap at low concentrations by allowing some electron hopping between all sites.

Returning to figure 9 we remark that the large increase in width of the impurity d level with concentration is of interest in the light of recent discussion concerning the relative importance of d-d overlap and s-d resonance in transition and noble metals. Anderson and McMillan (1967) as well as Heine (1967) argue that s-d resonance is the major source of the width of the d bands in a pure metal whereas Friedel (1969) stresses the importance of d-d overlap in a conventional tight binding scheme with s-d interaction regarded as a perturbation. The present results we feel support the latter point of view. If the width of the d band is the result of intra- rather than inter-atomic interactions, then one would expect the width of the Pd d level in Ag-rich alloys to be similar to that in pure Pd which is definitely not the case. By a similar argument one can ignore the possibility of the clustering of solute atoms giving rise to an impurity band split off from the d band of the host metal as has been proposed to explain the similar photoemission structure observed in CuNi alloys (Kidron 1969).

The half width of the Pd d level at infinite dilution estimated from figure 8 to be 1.0 eV arises from two principal sources, s-d resonance and spin-orbit interaction. Exchange splitting which is important for certain transition metal impurities, for example Mn, is not expected to be effective here nor is there evidence for it in the magnetic behaviour. Furthermore, to a good approximation, crystal field effects can be ignored; Mueller (1967) has pointed out that the cubic field gives rise to a splitting of less than 0.1 eV for pure Cu, any further influence of crystal structure causing a splitting of the d states with different symmetries is taken to be negligible. We assume that resonance of a d state with the conduction band will produce the Lorentzian density of bound state, Anderson (*loc. cit.*)

$$N_d = \frac{g}{\pi} \frac{\Delta}{(\epsilon - E_0)^2 + \Delta^2}$$

2Δ being the half value width, E_0 the mean position of the resonant level, and g the degeneracy of the level. However, in the present case one must allow for the spin-orbit splitting which gives rise to the $j = \frac{5}{2}$ and $j = \frac{3}{2}$ components to the 4d level. According to calculations by Herman and Skillman (1963) this splitting is 0.50 eV. In figure 10 we have attempted to fit the observed Pd structure with two Lorentzians centred at 1.9 and 2.4 eV and weighted in the ratio 3:2. Good agreement was obtained with $2\Delta = 0.5$ eV. The lower half of figure 10 compares the model curve broadened by experimental effects with the observed distribution for a 5% Pd alloy. The density of resonant bound state at the Fermi level, N_d , is marked on the curve and readily calculated to be 0.185 eV^{-1} per atom, a by no means insignificant quantity compared with the density of conduction states in pure silver 0.28 eV^{-1} per atom. Similarly we estimate the resonant d level to contain 9.62 ± 0.08 † electrons; in other words even the isolated Pd impurity atom dissolved in Ag contains ~ 0.38 holes, almost the same as in pure Pd.

This significant density of d states at small Pd contents provides a ready explanation of the initial increase in electron specific heat as Pd is added to Ag. Using the relation

† These limits are based on the Lorentzian and the liberal assessment $2\Delta = 0.5 \pm 0.1$ eV implying an uncertainty in the overall breadth of the observed resonance of ± 0.2 eV. The corresponding error in N_d is $\pm 0.035 \text{ eV}^{-1}$ per atom.

$\gamma_d = \frac{1}{3}\pi^2 k^2 N_d$, which ignores any possible phonon enhancement, the coefficient γ_d is found to be 0.43 mJK^{-2} per mole Pd. The experimental data of Montgomery *et al.* (*loc. cit.*) show that the γ of **AgPd** alloys increases linearly with Pd content and $d\gamma/dc = 0.24 \text{ mJK}^{-2}$ where c is the atomic concentration of Pd. This increase is however due to changes in the density of conduction states as well as d states and some allowance must be made for the former. This may be done empirically using the data for **AgCd** alloys (Montgomery *et al.*, *loc. cit.*). The addition of Cd to Ag causes an initial increase in electron heat according to $d\gamma/dc = 0.23 \text{ mJK}^{-2}$. If we now assume that the change in the density of conduction states in the immediate vicinity of the Fermi level is linear in electron content then, knowing that the relative valency of Pd in Ag is -0.62 , we can calculate the experimental value of γ_d for **AgPd** to be 0.39 mJK^{-2} per mole Pd. This is in excellent agreement with the value deduced directly from the photoemission data. Similar excellent agreement is also found in the case of **CuNi** alloys (Myers *et al.* 1969).

The experimental specific heat results show that the variation of γ is linear in Pd content up to at least 30%. On the other hand the resonant bound state of the Pd whilst broadening does not shift its position. We do not know how to take account of the broadening properly

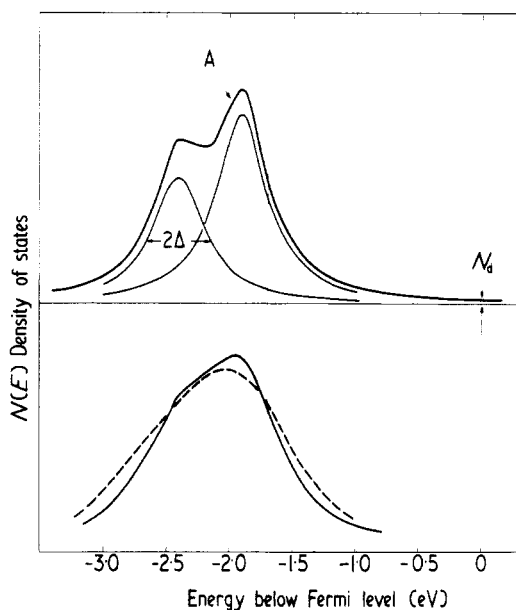


Figure 10. A model of the resonant bound 4d level of Pd in Ag. Curve A is the sum of two Lorentzian-shaped density of states functions. The lower half of the figure compares the model density of states broadened to allow for experimental effects with an actual measured curve. $2\Delta = 0.5 \text{ eV}$; $N_d = 0.185 \text{ eV}^{-1}$ per atom; $n_d = 9.62$ electrons; $n_d^+ = 0.38$ holes. Full curve, curve A (unbroadened); broken curve, $\text{Ag}_{0.95}\text{Pd}_{0.05}$.

but a simple procedure is to assume that the d-d interactions between Pd atoms cause an essentially symmetrical rectangular broadening and that the presence of s-d resonance maintains the Lorentzian distributions at the top and bottom of the level. On this assumption and knowing the observed total breadths as a function of Pd concentration, we can calculate the hole content and the density of resonant d state per atom at the Fermi level for different Pd contents. It is found that both quantities decrease rapidly and have

insignificant size at 40% Pd—see figure 11. The observed linear variation of γ with Pd content must, we feel, be attributed to changes in both γ_d and the corresponding quantity for the conduction states, a decrease in the former being compensated by an increase in the latter. This is not unlikely since the Fermi level for Ag lies between the L and X points in the Brillouin zone and although an initial decrease in conduction electron concentration may cause a decrease in conduction state density a continued depletion of conduction electrons should certainly lead to an eventual increase. Experiment shows that the net result is an electron heat which increases linearly with Pd content.

It will be noted that the number of electrons contained in the resonant level of the isolated Pd impurity atom is $n_d = 9.62$ which is not far removed from the occupation number of the 4d states of the isolated atom. We can compare this situation with the CuNi alloys (Seib and Spicer 1968, Myers *et al.* 1969) where the isolated Ni impurity atom in Cu has ~ 8.5 d electrons and the lowest terms in the isolated free atom are $3d^8$ and $3d^9$. In the case of Ni the spin-orbit splitting is to a good first approximation insignificant and for the isolated Ni impurity in Cu one finds $2\Delta = 1$ eV. The difference in resonant level widths for the two cases of Pd in Ag and Ni in Cu may be associated with the different conduction electron contents in the appropriate Pd and Ni cells; the former contains 0.38 the latter 1.5 conduction electrons and the d states resonate with the local conduction electron density; this aspect will be considered again later.

4.2.2. *Pd-rich alloys.* The photoemission data show that the d levels in pure Pd occupy a band more than 4 eV broad and this is consistent with recent band structure calculations (Krogh-Andersen 1969) which suggest that the deepest d band at the X symmetry point lies 5.3 eV below the Fermi level. However, experiments with larger photon energies are needed to expose the complete d band. Characteristic for Pd is its large electron specific heat $\gamma = 9.5 \text{ mJ K}^{-2}$ per mole, it is however difficult to convert this into a density of states since the effect of phonon and spin fluctuation enhancement are not accurately known. However, the calculations of Krogh-Andersen suggest that the total enhancement cannot be very different from 2 and we shall arbitrarily assume the factor 2. Thus in pure Pd we expect $N_d \sim 2 \text{ eV}^{-1}$ per atom, the contribution of the conduction electrons to this value being for present purposes negligible. Associated with the large value of N_d is the large exchange-enhanced Pauli paramagnetism. Both the electron heat and paramagnetic susceptibility decrease almost linearly as Ag is added to Pd a distinct break in behaviour occurring at about 60% Ag where the alloys become diamagnetic and the electron heat attains a value typical of an ordinary metal. The experimental data of figure 3 illustrate this variation of the density of states at the Fermi level. These facts are readily explained on the basis of the rigid band or virtual crystal models but falsely so.

In attempting to explain the observed behaviour there are at least two aspects worthy of consideration and these are the effects of structural disorder caused by alloying and the local densities of states at the Fermi level in the Pd and Ag atomic cells. Consider first the isolated Ag impurity atom dissolved in Pd. The Ag d levels might conceivably form a truly localized bound state if they lay beneath the local conduction band, but since they lie above the lowest 5s state in the free atom, this is very unlikely; in all probability they form a narrow resonant bound doublet and although this, of necessity, will have a finite density at the Fermi level, it will be insignificant quantitatively. Thus neglecting any slight changes in the conduction band states, the effect of adding Ag to Pd will be one of pure dilution. But this is much less than the real effects observed. Pure dilution requires that each Ag atomic cell contain one conduction electron and this in turn implies that there is a total density of state at the Fermi level $N(\epsilon_0) \sim 0.28 \text{ eV}^{-1}$ per atom whereas around each Pd atom the corresponding quantity is $\sim 2 \text{ eV}^{-1}$ per atom. This large difference in state density between the Ag and Pd cells is incompatible with complete self-screening of the Ag impurity atom; this is readily appreciated on the basis of the simple Thomas-Fermi approximation. In fact the extra nuclear charge introduced with each Ag atom will, on account of the locally low value of $N(\epsilon_0)$ compared with that of the matrix, be weakly screened and it will therefore be felt by the neighbouring Pd atoms; the d states on these

atoms will be pulled down relative to the Fermi level which in the first approximation will remain unchanged. The empty levels pulled down by the weakly screened impurity potential will be preferentially occupied by a proportion of the impurity conduction electrons. The resultant effect is a transfer of Ag conduction electrons to Pd d states, the Ag d states not entering the process at all; furthermore since the above impurity effect will be proportional to the effective impurity charge, it should be dependent on the valency of the impurity atom.

Regarding the effects of disorder these are clearly seen in our experimental data. The top of the d band of pure Pd is characterized by a very sharp peak and the Fermi level lies on the high energy side of the peak. Its sharpness arises for symmetry reasons, the states in question not being hybridized with the conduction band. The broadening of this peak with the addition of Ag to Pd is clearly seen in figure 4 and is partly due to the natural weakening of Van Hove singularities with increasing disorder but also due to the fact that the disorder should cause a mixing of the initially unhybridized d states with the conduction states. Any effects of disorder will be a result of the perturbation of the lattice potential; the range of the perturbation will be connected directly with the Friedel oscillations in screening charge and the strength of the perturbation proportional to the difference in atomic number between host and impurity atoms. Thus the two contributory mechanisms to the reduction of d state density at the Fermi level, electron transfer and structural disorder are two aspects of the same phenomenon which we may describe as Friedel screening. A similar explanation almost certainly applies to the NiCu, NiZn, NiAl and other Ni alloys; any small effect due to possible differences in initial density of conduction states on the different impurity atoms being small compared with the difference between the Ni and the impurity atoms—and of course the difference in atomic number.

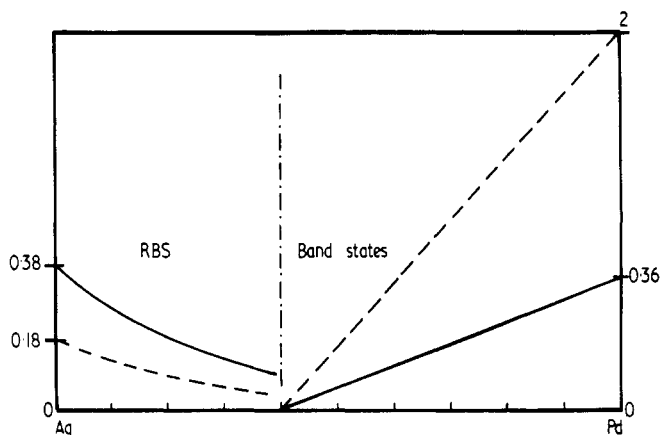


Figure 11. Possible variation of the number of d holes (full curves) and d state density at the Fermi level, (broken curves) for AgPd alloys. The two distinct regions appropriate to resonant bound states and band states are apparent. The values for the resonant bound state (RBS) were calculated on the assumption of rectangular broadening as described in the text.

The above proposal provides we believe a good physical process for the decrease in state density at the Fermi level as Ag is added to Pd; since Ag conduction electrons are transferred to Pd d states the number of d state holes must necessarily decrease and the variation of both electron heat and susceptibility indicates that this decrease occurs in an essentially linear fashion between 0 and 60% Ag. In figure 11 we have attempted to illustrate how the density of d states at the Fermi level and the number of d state holes, both quantities wholly associated with the Pd atoms, vary throughout the alloy system. The diagram shows two

distinct regions where the resonant bound state and the true band states are operative for the Pd 4d levels. Moreover the diagram as well as the photoemission data of figure 3 imply that the change from one description to the other is sharp rather than gradual. The impression is that the perturbation of a Pd atom by neighbouring ones, as more and more Pd is added to Ag, although causing a broadening of the resonant d levels, is not sufficient to change their essentially resonant character. The resonant state remains until a critical concentration of Pd is reached at which sufficiently many Pd atoms are interacting to cause a transition to a true collective band structure in which d-d overlap becomes the overriding mechanism and s-d resonance a perturbation. We suggest that this change from one description of the d levels to the other is a cooperative transition and may be described as a 'semiconductor-metal' transition for the d electrons of the Pd. It is significant in this connexion that as far as we are aware all the measured physical properties of AgPd alloys, whilst varying in a continuous manner with composition, show discontinuities in the gradients with composition in the region 55%–60% Ag. It is unlikely that a similar transition will occur in the case of the 4d electrons of Ag since these most probably lie within the energy range of the Pd d band. Thus in addition to s-d resonance broadening, which we expect to be small since the Ag d levels lie so low, there will be the effect of inter-atomic d-d broadening between Ag and Pd neighbours. In any event the Ag d electrons are always so far below the Fermi level they do not produce any measurable effect on the properties of the alloys.

4.3. Residual electrical resistance

The residual electrical resistance of the AgPd alloys has a characteristic departure from the parabolic curve expected on the basis of Nordheim's rule. Mott (1936) gave an explanation in terms of s-s and s-d scattering processes, the latter being dominant in the Pd-rich alloys. Coles and Taylor (*loc. cit.*) showed that the rigid band model, assuming 0.6 d holes per Pd atom in pure Pd could be fitted accurately to the experimental data. Dugdale and Guénault (*loc. cit.*) modified the model to take account of Vieullmin and Priestley's (1966) finding that the number of d holes per atom in pure Pd is 0.36 and not 0.6 as supposed by Mott. They assumed that the number of 4d holes per Pd atom varied linearly from 0.36 in pure Pd to 0 for 55%. The major assumption that the number of d state holes was the significant variable was maintained. The scattering processes giving rise to electrical resistance are, amongst other things, dependent on the density of states at the Fermi surface and whereas the existence of a d state density requires d state holes a given small quantity of the latter can be associated with either a low or a high state density dependent upon whether the d states occur as resonant bound states or true collective band states. Following Dugdale and Guénault, it may readily be shown that our description of the electron states in AgPd alloys allows an accurate representation of the experimental residual resistivity. Furthermore we can estimate the contribution of the impurity d state to the resistivity. Following the treatment of Friedel in terms of phase shifts, we calculate the initial change in resistivity of Ag due to the presence of Pd d states to be $13 \mu\Omega \text{ cm}$ per mole Pd. To this must be added a component due to the reduced conduction electron content. For this purpose we consider Pd in Ag to have valency 0.38 and use Linde's rule together with the known resistivity data for Ag-Cd alloys to calculate a contribution $15 \mu\Omega \text{ cm}$ per mole Pd. The total impurity resistivity is therefore $28 \mu\Omega \text{ cm}$ per mole Pd; this is somewhat less than the observed value of $44 \mu\Omega \text{ cm}$ per mole Pd. In the analogous CuNi alloys a similar calculation gives better agreement. The extra resistivity in this case arises wholly from the resonant d state, we calculate a value $154 \mu\Omega \text{ cm}$ per mole Ni whereas measurement gives $129 \mu\Omega \text{ cm}$ per mole.

5. The Anderson parameters

In the Anderson model the width of the resonant bound state is given by the following expression

$$\Delta = \pi \langle V^2 \rangle N_d(\epsilon)$$

where $\langle V^2 \rangle$ is the average value of the square of the s-d interaction potential. Our data for Δ could be used to calculate V if $N_g(\epsilon)$ the appropriate conduction state density were known. The value of $N(\epsilon)$ required is that for electrons of given spin on the Pd site at an energy corresponding to the centre of gravity of the resonant bound state, the latter lies 2.1 eV below the Fermi level in the case of Pd dissolved in Ag. However, the form and breadth of the conduction band at a Pd site are unknown. It is clear however that the number of occupied electron states, 0.38 per atom, demands that the band breadth be smaller or the band form shallower than is the case for Ag. In the case of pure Ag a combination of theoretical calculation (Christensen 1969) and experimental data suggests that the conduction band breadth is 7.23 eV and the conduction density of state at the Fermi level 0.28 eV⁻¹ per atom. Calculations by Krogh-Andersen (1969) show that the corresponding quantities for pure Pd are 7 eV and 0.25 eV⁻¹ per atom. The d bands cause appreciable distortion of the conduction band from the form expected on a free electron basis. The free electron band breadth for conduction states associated with a Pd impurity atom in Ag is readily calculated to be 2.9 eV. The impurity resonant d state has effective total breadth 2 eV whereas in pure Pd metal the d band is probably 5.5 eV wide. Assuming the distortion of the conduction band to be directly proportional to the d band breadth and working from the data for pure Pd, we estimate the band breadth for the conduction electron around the single Pd impurity atom in Ag to be 4.4 eV. The centre of the resonant impurity d state probably lies therefore at an energy ~ 2.3 eV above the bottom of the local conduction band which on a free electron approximation corresponds to a conduction electron density of state equal to 0.165 eV⁻¹ per atom; this is probably an upper estimate since the true conduction bands are 'thinned down' by the d states. Remembering that the value 0.165 eV⁻¹ per atom corresponds to both spin directions together, a value 1.19 eV is found for the parameter V . As stated above, this is probably an upper limit, however even if the appropriate state density were considerably smaller say, 0.10 eV⁻¹ per atom, the value of V only becomes 0.8 eV. We feel that it is very unlikely that V departs greatly from a value of approximately 1 eV and that the true value probably lies in the range 1 ± 0.2 eV. This is considerably less than the original estimates made by Anderson but our measured widths are also much less than his original suggestions. The value of V is in good agreement with other estimates (Heeger 1969). It is also of the correct size to account for the changes in conduction electron behaviour due to perturbation by d states, as for example in pure Cu (Friedel 1969).

We have already noted that in the CuNi alloys the Ni resonant d level has width twice that observed for the corresponding level for Pd in Ag. This may be due to some distinct difference in the parameter V . However, the local density of conduction electrons in the Ni cell is ~ 1.5 compared with 0.38 in the case of Pd. This difference is probably sufficient to account for the major part of the difference in level breadths without invoking any change in V .

6. Summary and conclusions

Photoemission experiments on AgPd alloys have shown that for Ag-rich alloys the d electrons of the two components lie well separated in energy and interact only slightly with one another. The Pd d electrons form a resonant bound state lying between the top of the Ag d band and the Fermi level. At vanishing Pd concentration the width of this bound state has been accounted for partly by spin-orbit splitting and partly by a true resonance broadening, the latter corresponding to an s-d mixing potential in the range 1 ± 0.2 eV. The increase in breadth with increasing Pd content was attributed to Pd d-d interatomic interactions and is probably accompanied by a decrease in the number of d holes and a reduction in the density of d state at the Fermi level. Apart from the complications of s-d resonance one may picture the alloying of Pd with Ag as the addition of d electrons to an empty lattice; the localized character of the state is then maintained up to concentrations approaching 40% Pd but beyond this value the d electrons of the Pd occupy true band states.

The idea of a local density of states has been invoked to describe the screening of Ag atoms dissolved in Pd. This results in a transfer of electrons from Ag conduction states to Pd d states thereby causing the characteristic decrease in electron specific heat and paramagnetic susceptibility. The same concept was used to discuss the different resonant state widths observed in AgPd and CuNi alloys.

The effect of structural disorder on the form of energy bands has been clearly demonstrated. The sharp profiles of the d bands of pure Ag and pure Pd become quickly blurred by alloying.

Direct transitions between conduction band states, Λ_1 - Λ_1 transitions, were observed only in the most dilute AgPd alloy (5% Pd). The observed movement of the transition is in good agreement with band structure calculations for Ag.

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