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# Optical properties of coloured platinum intermetallic compounds

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The optical properties of the intermetallic compound $PtAl_2$ were altered by the addition of 5% –25% copper by mass. It was found that these additions cause the colour of the compound to change from the brass-yellow of $PtAl_2$ through orange to copper-pink. The colour of the intermetallic compounds has been described using the CIELab and chromaticity colour-measuring systems. The effect of the copper additions on the lattice parameter and band structure is discussed, related to the associated change in colour of the intermetallic compound. The effect of the copper additions on the physical and mechanical properties of the material has been studied.

## 1. Introduction

It has been known for some time that many intermetallic compounds containing platinum-group metals (PGMs) have reflection coefficients that are strongly dependent on wavelength in the visible region of the spectrum, and are therefore coloured. Apart from the inherently interesting properties of these materials, they have attracted interest because they have potential applications as opto-electronic components, as selective solar absorbers, and in jewellery and other decorative arts. The first mention of these compounds seems to have been by Campbell and Matthews [1]. Savitskii [2] refers to various compounds of this type. Schuster and co-workers (see, for example, [3–7]) have investigated a large number of ternary and quaternary compounds containing PGMs. Many of these compounds have the fluorite cF12 (or closely similar) structure. Recently, Chen and Lynch [8] compared the optical properties of $PtAl_2$ with those of $AuAl_2$, and interpreted these in terms of a theoretical band structure calculated for $AuAl_2$.

This paper reports the optical and other properties of $PtAl_2$ containing up to 25% copper by mass [9]. $PtAl_2$ has the simple fluorite structure. The addition of copper to the level mentioned changed the lattice parameter, but not the structure. The paper also discusses some properties of other samples containing more copper, and varying platinum and aluminium contents. Some of these samples were alloys rather than intermetallic compounds.

## 2. Experimental procedure

### 2.1. Sample preparation

All samples were prepared in a laboratory-scale plasma-arc furnace, using a protective argon atmosphere. Melting was carried out on a water-cooled copper hearth. For samples containing less than 27% copper (all compositions refer to mass per cent, unless otherwise stated), pieces of previously prepared $PtAl_2$ were melted together with the target amount of copper. Other samples were usually prepared by melting together the target amounts of platinum, aluminium, and copper.

### 2.2. Optical measurements

Optical measurements were carried out with a Spectrogard reflection spectrophotometer. A standard CIE source C illuminant was used, approximating average daylight conditions. A CIE standard observer angle of 2° was used throughout. Both the chromaticity $Yxy$ and CIELab colour coordinates $a^*$ and $b^*$ were calculated from the measured data. The specular component of the reflected light was included in the calculations. The percentage reflectivity of the samples was measured in the wavelength range 450–900 nm. For the optical measurements, samples were mounted and polished to a mirror finish, using 1μm diamond powder.

### 2.3. Lattice parameter measurements

X-ray diffraction (XRD) measurements were carried out with a Siemens diffractometer, on samples containing less than 30% copper. Although the relative intensities of the diffraction peaks changed with the copper content, the basic fluorite structure of the $PtAl_2$ remained unchanged. The lattice parameter for each sample was found by calculating the average value determined from nine lines.

### 2.4. Chemical composition of phases

The chemical composition of individual phases in the samples was determined with a Joel Super Probe electron-microprobe analyser. Although many of the samples appeared optically homogeneous to the naked eye, some of them consisted of distinct separate phases with different colours on a microscopic scale.

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TABLE I Sample composition and colour coordinates

| Sample no. | Composition (mass %) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Pt | Al | Cu | $x$ | $y$ | $L^*$ | $a^*$ | $b^*$ | Colour(%) | Colour[a] |
| 1. Platinium | 100 | | | 0.32 | 0.32 | 89.12 | − 0.13 | − 0.54 | 4.12 | |
| 2. PtAl | 87.8 | 12.2 | | 0.32 | 0.32 | 82.93 | 1.86 | 2.28 | 3.58 | |
| 3. $Pt_2Al_3$ | 83 | 17 | | 0.31 | 0.32 | 78.34 | − 1.41 | 1.93 | 2.57 | |
| 4. $PtAl_2$ | 77 | 23 | | 0.35 | 0.35 | 83.91 | 0.67 | 17.71 | 20.14 | yel |
| 5. $PtAl_2$ + 2%Cu | 75.5 | 22.5 | 2 | 0.34 | 0.35 | 80.45 | 0.43 | 14.45 | 17.13 | yel |
| 6. $PtAl_2$ + 5%Cu | 73.2 | 21.8 | 5 | 0.37 | 0.37 | 79.05 | 0.56 | 26.85 | 31.45 | yel |
| 7. $PtAl_2$ + 6%Cu | 72.4 | 21.6 | 6 | 0.37 | 0.37 | 78.71 | 2.28 | 24.08 | 28.72 | yel |
| 8. $PtAl_2$ + 7%Cu | 71.6 | 21.4 | 7 | 0.36 | 0.36 | 79.5 | 1.93 | 22.17 | 26.32 | yel |
| 9. $PtAl_2$ + 8%Cu | 70.8 | 21.2 | 8 | 0.36 | 0.36 | 79.7 | 2.42 | 20.98 | 25.04 | yel |
| 10. $PtAl_2$ + 9%Cu | 70.1 | 20.9 | 9 | 0.36 | 0.36 | 79.9 | 2.61 | 22.12 | 26.30 | org/yel |
| 11. $PtAl_2$ + 10%Cu | 69.3 | 20.7 | 10 | 0.36 | 0.36 | 79.06 | 4.07 | 22.02 | 26.69 | org |
| 12. $PtAl_2$ + 15%Cu | 65.5 | 19.5 | 15 | 0.36 | 0.34 | 75.33 | 10.07 | 13.62 | 19.08 | org/red |
| 13. $PtAl_2$ + 20%Cu | 61.6 | 18.4 | 20 | 0.34 | 0.33 | 75.7 | 7.89 | 9.25 | 13.41 | cop/red |
| 14. $PtAl_2$ + 25%Cu | 57.8 | 17.2 | 25 | 0.34 | 0.33 | 77.44 | 7.63 | 7.76 | 11.38 | cop/red |
| 19 | 54 | 16 | 30 | 0.34 | 0.33 | 78.87 | 5.37 | 8.20 | 11.25 | org |
| 20 | 50 | 15 | 35 | 0.34 | 0.34 | 73.75 | 5.01 | 9.94 | 13.89 | org |
| 22 | 77 | 8 | 15 | 0.32 | 0.33 | 76.32 | 0.35 | 4.22 | 5.74 | p.yel/org |
| 24 | 81 | 9 | 10 | 0.32 | 0.32 | 66.88 | 0.66 | 3.62 | 5.61 | p.yel/org |
| 26 | 78 | 12 | 10 | 0.31 | 0.32 | 75.17 | 0.04 | 2.007 | 3.15 | p.yel |
| 27 | 74 | 11 | 15 | 0.32 | 0.32 | 77.45 | − 0.90 | 3.37 | 4.41 | p.yel |
| 28 | 65 | 10 | 25 | 0.32 | 0.33 | 78.91 | − 0.38 | 4.23 | 5.42 | p.yel/org |
| 29 | 56.5 | 8.5 | 35 | 0.32 | 0.33 | 76.37 | − 0.10 | 4.42 | 5.85 | p.yel/org |
| 30 | 50.5 | 7.5 | 42 | 0.32 | 0.33 | 81.81 | 0.44 | 4.63 | 5.93 | p.pnk/org |
| 31 | 78 | 17 | 5 | 0.32 | 0.33 | 75.07 | − 0.15 | 4.34 | 6.09 | p.yel |
| 32 | 74 | 16 | 10 | 0.33 | 0.33 | 76.5 | 0.77 | 6.40 | 8.38 | p.yel/org |
| 33 | 69.5 | 15.5 | 15 | 0.33 | 0.33 | 76.09 | 2.81 | 7.22 | 9.87 | org/yel |
| 34 | 65.5 | 14.5 | 20 | 0.32 | 0.32 | 78.75 | 0.30 | 3.72 | 4.99 | org/yel |
| 36 | 61 | 29 | 10 | 0.33 | 0.33 | 73.81 | 3.46 | 5.46 | 7.98 | p.org/pnk |
| 37 | 57.5 | 27.5 | 15 | 0.33 | 0.33 | 71.85 | 4.02 | 6.65 | 9.87 | org/pnk |
| 38 | 54.5 | 25.5 | 20 | 0.33 | 0.33 | 73.13 | 3.75 | 7.12 | 10.24 | org/pnk |
| 39 | 69 | 26 | 5 | 0.33 | 0.33 | 74.14 | 2.90 | 6.38 | 9.04 | org/yel |
| 45 | 70 | 2.5 | 27.5 | 0.32 | 0.32 | 76.68 | − 0.22 | 2.55 | 3.61 | p.yel |
| 46 | 50 | 8 | 42 | 0.33 | 0.33 | 81.52 | 0.47 | 7.70 | 9.37 | p.yel |
| 47 | 50 | 4 | 46 | 0.33 | 0.33 | 82.29 | 1.67 | 7.92 | 9.82 | p.yel/org |
| 48 | 50 | 8 | 42 | 0.32 | 0.33 | 81.43 | 0.81 | 6.54 | 8.17 | p.yel/org |
| 49 | 50 | 4 | 46 | 0.33 | 0.33 | 80.1 | 0.86 | 7.37 | 9.21 | p.yel/org |
| 50 | 58 | 8 | 34 | 0.32 | 0.33 | 81.18 | 0.05 | 4.87 | 6.14 | p.yel |
| 51 | 50 | 4 | 46 | 0.33 | 0.33 | 79.11 | 1.72 | 8.95 | 11.31 | p.yel/org |
| 52 | 58 | 8 | 34 | 0.32 | 0.33 | 79.81 | − 0.19 | 4.51 | 5.77 | p.yel |

[a] yel = yellow, org = orange, cop = copper, pnk = pink, p.pnk = pale pink, p.yel = pale yellow.

### 2.5. Melting point and hardness measurements

As mentioned in the introduction, a potential application of the compounds investigated here is in jewellery. The melting point of the compounds is therefore of practical importance. The melting points of several of the compounds were measured by standard differential thermal analysis (DTA) techniques, using Setaram equipment.

Hardness and brittle fracture of the samples could also be of importance for some applications. Microhardness measurements were carried out with a Shimadzu microhardness tester. In some cases the lengths of the cracks at the corners of the hardness indentations were measured in order to make a semi-quantitative estimate of the fracture toughness.

## 3. Results

### 3.1. Optical measurements and colour coordinates

The compositions of the samples and the results of the colour measurements are summarized in Table I. The meaning of the symbols will be explained shortly. Samples 4–14 constitute the series in which copper was melted together with pre-alloyed $PtAl_2$ fragments. It can be seen that the effect of an increase in the copper content is to change the colour from the characteristic brass-yellow of $PtAl_2$ through orange to copper-red. Fig. 1 gives percentage reflectivity as a function of wavelength for $PtAl_2$ (Sample 4) and other samples containing varying amounts of copper. It is clear that the effect of an increase in copper additions is to progressively lower the percentage reflectivity for wavelengths above about 500 nm (i.e. photon energies below about 2.4 eV). We cannot explain the sharp drop in the minimum of the reflection curve for the sample containing 2% copper by mass.

By plotting the chromaticity coordinates ($Yxy$) in the standard colour locus [10], a graphical representation of the colour of the samples is obtained, relative to other known materials. An expanded plot for the various samples is given in Fig. 2. Gold and copper are also plotted for comparison purposes. The $x$ and $y$

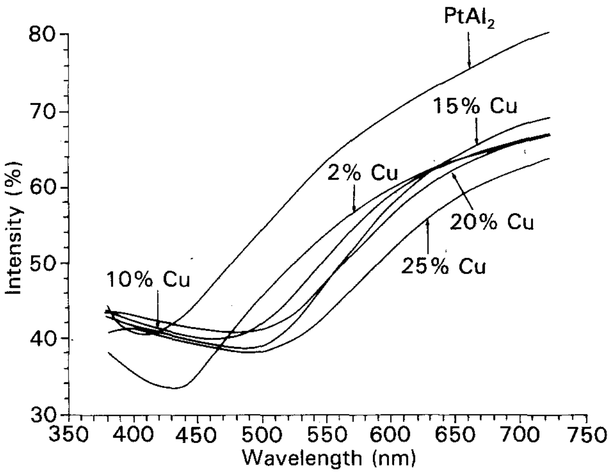

*Figure 1* Reflectivity curves for PtAl$_2$ and PtAl$_2$ + Cu.

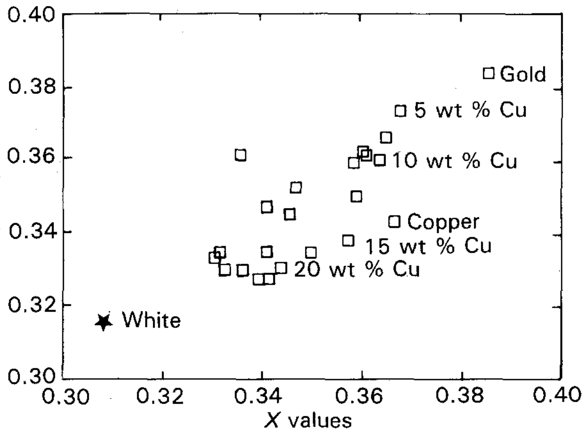

*Figure 2* Expanded colour locus.

values for the individual samples are listed in columns 6 and 7 of Table I.

The colour saturation of the samples can be calculated by the determination of the position of each sample on the graph, relative to the white point and the 100% colour-saturation point on the perimeter of the colour locus. These values are given in column 11 ("% colour") of Table I. For comparison purposes, it may be mentioned that colour-saturation values for typical 18, 14, and 9 carat gold alloys are 26.4%, 22.9% and 14.9%, respectively. The colour-saturation values for the PtAl$_2$ samples containing up to 25% copper range from 31.5% for the 5% copper sample 6%–11.4% for the 25% copper Sample 14. These values compare favourably with those of the gold alloys.

An alternative method of representing the colour of the compounds is to plot contours of equal $a^*$ and $b^*$ values in the CIELab system [11] on a composition triangle. The values for $a^*$ and $b^*$ are given in columns 9 and 10 of Table I. The $a^*$ coordinate is a measure of the intensity of the red and green colours of the sample: an increasingly positive $a^*$ indicates more red in the sample, and increasingly negative $a^*$ values indicate more green. Similarly, $b^*$ measures yellow and blue: increasingly positive $b^*$ indicates more yellow, and increasingly negative $b^*$ more blue.

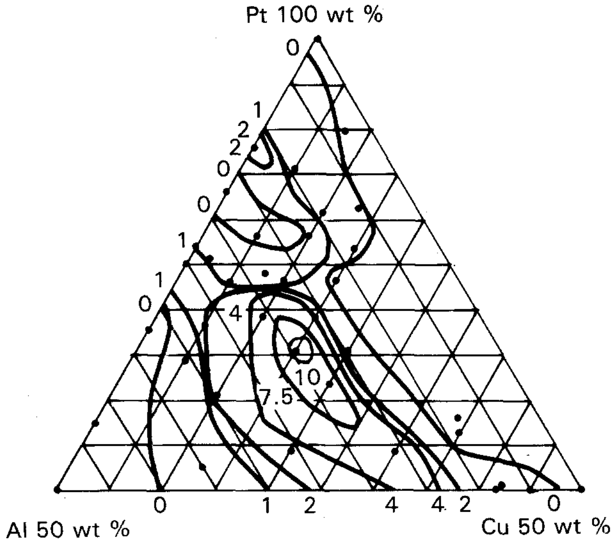

*Figure 3* Contours of equal values of $a^*$, where an increase in the $a^*$ value indicates an increase in red component.

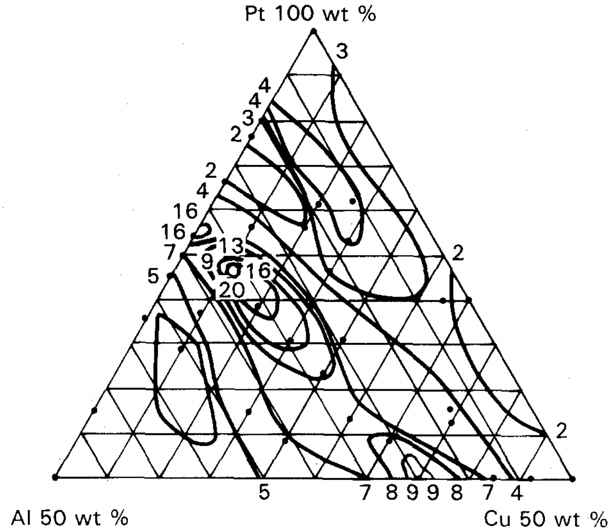

*Figure 4* Contours of equal values of $b^*$, where an increase in the $b^*$ value indicates an increase in the yellow component.

Figs 3 and 4 give contours of equal $a^*$ and $b^*$ values, respectively, plotted on composition triangles. It can be seen that the compositions of highest colour saturation occur in the region of PtAl$_2$ plus 0%–30% copper. The samples with the highest yellow component (17–26) are those containing 0%–5% copper. The yellow component decreases in both the horizontal and vertical directions from this composition range. The highest red component of 10 units is found at 15% copper. Again, the red component decreases in both the horizontal and vertical directions as we move away from this composition.

## 3.2. Lattice parameter measurements

As mentioned earlier, the addition of up to 25% copper by mass does not change the basic fluorite structure of PtAl$_2$. However, the lattice parameter increases with copper content. The lattice parameter is plotted against the copper content in Fig. 5. Standard linear least-squares regression gives the trend line

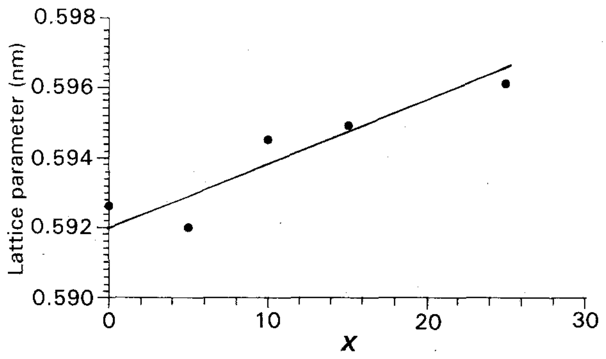

*Figure 5* Lattice parameter of $PtAl_2 + X\%$ Cu by mass.

TABLE II Microprobe analyses

| Sample | Pt | Al | Cu | |
|---|---|---|---|---|
| 4. $PtAl_2$ | 77.0 | 23.0 | | mass % |
| | 31.6 | 68.4 | | at % |
| 11. Orange | 74.0 | 17.5 | 8.5 | mass % |
| | 32.7 | 55.8 | 11.5 | at % |
| 14. Pink | 68.0 | 16.0 | 16.0 | mass % |
| | 29.2 | 49.7 | 21.1 | at % |
| 14. White | 21.5 | 14.5 | 64.0 | mass % |
| | 6.6 | 32.5 | 60.9 | at % |

shown, which corresponds to

$$\text{lattice parameter (pm)} = 592.0 + 0.198x \quad (1)$$

where $x$ is the copper content of the sample in mass per cent.

## 3.3. Microprobe analysis of phases

The samples analysed with the electron microprobe were Samples 4–14. In Sample 14 (25% copper by mass), a pink phase dominated when the sample was viewed under the microscope. There was also a significant amount of a white phase present. Sample 11 contained an orange phase as the dominant phase, together with a white phase. (However, there was considerably less of the white phase present than in Sample 14.) Microprobe analyses of these three phases, together with an analysis of nominally pure $PtAl_2$, are given in Table II.

## 3.4. Hardness values

Vickers microhardness values are shown as a function of composition in Fig. 6. Values for the intermetallic compounds range from about 600–920. There is a trend for the samples with higher copper contents to have lower hardnesses, but even these are very high. The much lower values long the Pt–Cu binary line correspond to alloys. The lengths of cracks at the corners of Vickers hardness indentations may be used to estimate fracture toughness semi-quantitatively (see [12, 13]). An attempt was made to do this in the present work, in order to determine whether fracture toughness improved at the higher copper contents. The results were not very conclusive. In order for cracks to be present at all, the material has to be extremely brittle, and this technique is therefore only a measure of the degree of brittleness because all samples are inherently brittle.

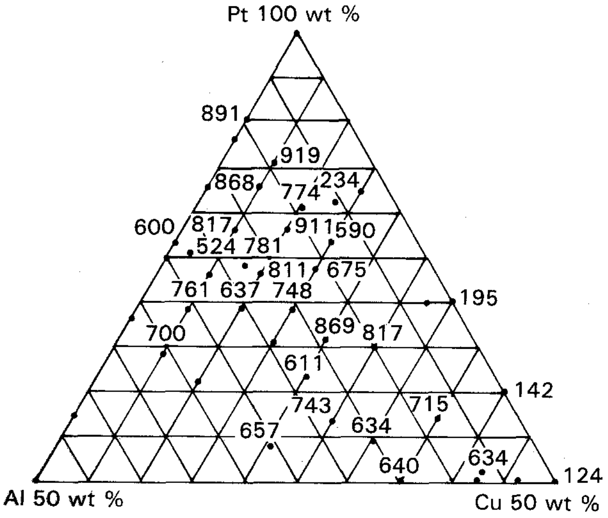

*Figure 6* Vickers microhardness as a function of composition.

TABLE III Melting-point data

| Sample | Melting point (°C) |
|---|---|
| 4. ($PtAl_2$) | 1414 |
| 5. ($PtAl_2$ + 2%Cu) | 1324 |
| 6. ($PtAl_2$ + 5%Cu) | 1406 |
| 11. ($PtAl_2$ + 10%Cu) | 1380 |
| 12. ($PtAl_2$ + 15%Cu) | 1352 |
| 13. ($PtAl_2$ + 20%Cu) | 1335 |
| 14. ($PtAl_2$ + 25%Cu) | 1288 |
| 19[a] | 1179 |
| 20[a] | 1210 |
| 51[a] | 1121 |

[a] see Table I.

## 3.5. Melting points

The melting points determined by the DTA technique are given in Table III.

## 4. Discussion

As the copper content of $PtAl_2$ increases, the colour changes from brass-yellow through orange to pink. The reason for the colour change is clear from Fig. 1. The sample containing 25% copper has a minimum in the green region of the spectrum (about 500 nm), and the higher reflectivity at the blue and particularly red ends of the spectrum combine to give the characteristic pink/mauve colour.

It is clear from Fig. 5 that the colour change is associated with an increase in the lattice parameter. For the sample containing 25% copper (the pink/mauve sample), the lattice parameter is about 0.8% greater than that of pure $PtAl_2$. This result is strikingly similar to that obtained for the compound $Li_2PdSn$

by Drews *et al.* [7]. This compound is also brass-yellow. By progressively adding magnesium to the compound (which displaces lithium on an atom-by-atom basis), the colour changes through copper-red to mauve, while the lattice parameter increases by about 1.6%. $Li_2PdSn$ has a crystal structure that is closely related to the fluorite structure of $PtAl_2$.

Before the possible electronic origins of the change are discussed, the question of whether the added copper substitutes for platinum or for aluminium in the $PtAl_2$ lattice is considered. Both X-ray diffraction and microanalysis data will be used for this purpose.

The substitution of copper for either of the other two elements would lower the symmetry of the structure, and result in the appearance of X-ray diffraction lines that are normally forbidden. The relative intensities of the lines normally present in $PtAl_2$ would also be changed.

A computer program, POWD10, was used to predict line intensities for a sample with a high copper content, both for the case where copper substituted for platinum and where it substituted for aluminium. The predicted values were then compared with the experimental diffraction traces. Although the comparison slightly favoured the copper-for-aluminium case, the results were not unambiguous enough to be conclusive.

However, examination of the electron microprobe results clearly indicates the substitution of copper for aluminium. This is most easily seen by examination of the atomic percentages for the various phases in Table II. The atomic percentage of platinum in both the orange and pink phases is close to that for $PtAl_2$. However, the atomic percentage of aluminium in both these phases has been reduced by about the atomic percentage of copper in the phase. The missing aluminium, and the fact that the copper content of Sample 14 is less than expected, could be accounted for by small amounts of the "white" phase, which is most likely predominantly an aluminium–copper alloy of variable composition (see Table II).

The sum of the effective radii of platinum and aluminium in $PtAl_2$ is equal to one quarter of the body diagonal of the full cF12 unit cell of $PtAl_2$. If the lattice parameter is taken as 592 pm, the sum of the radii is 213 pm. The use of the accepted atomic radius of 139 pm for platinum yields an effective radius of 74 pm for aluminium. This is reasonable, and lies somewhat above the 50 pm radius of the trivalent aluminium ion, and well below the 143 pm atomic radius of aluminium. Copper has radii of 69 and 96 pm for the mono- and divalent ions, respectively. Simple comparison of these values with the 50 pm for the aluminium ion indicates that the substitution of copper for aluminium would dilate the lattice, as was observed.

The changes in the reflection spectrum of $PtAl_2$ produced by the copper additions will now be discussed. As mentioned in the introduction, Schuster and his co-workers investigated the reflectivity of a large number of ternary and quaternary compounds containing gold or PGM [3–7]. Most of these had the cF12 structure, like $PtAl_2$, or a closely related structure. Colour in these compounds is due to prominent absorption (and a corresponding increase in reflection) at energies above a threshold that is typically in the range 2–3 eV. (Corresponding wavelengths are about 600–400 nm). In the discussion of their results, these authors tend to favour the excitation of electrons from a d-band to the Fermi level as the source of this absorption.

More recently, Chen and Lynch [8] have carefully analysed the results of optical measurements on $PtAl_2$ and $AuAl_2$. They interpreted these results with the aid of a band structure for $AuAl_2$ calculated by Switendick and Narath [14]. They concluded that, at least for gold and platinum di-aluminide, the source of the strong increase in reflectivity above 2.2 eV ($AuAl_2$) and 2.8 eV ($PtAl_2$) was the transitions between s- and p-bands and the Fermi level. They also concluded that the reflectivity at *lower* energies (higher wavelengths) in $PtAl_2$ was too high to be accounted for by Drude electrons alone, so that there was a contribution from interband transitions in this region as well.

Examination of Fig. 1 shows that an increasing copper content in the $PtAl_2$ samples produces a progressive lowering of the reflectivity (and associated absorption) at the longer wavelengths in the visible region of the spectrum. If the Chen and Lynch hypothesis is accepted, this lowering could be due to a lowering of the Fermi level with increasing copper content, and the consequent reduction of the interband absorption in this region. The lowering of the Fermi level is quite plausible when one bears in mind that the progressive substitution of copper for aluminium reduces the average number of valence electrons per formula unit in $PtAl_2$. However, small changes in band energies caused by the presence of copper and the small increase in the lattice parameter might also play a (probably less important) role.

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