effective impurity potential accounting for electron screening is given by

$$v(\boldsymbol{q}) = v_0(\boldsymbol{q})/\varepsilon(\boldsymbol{q}) . \tag{5}$$

Here $v_0(\boldsymbol{q})$ is the Fourier transform of $v_0(\boldsymbol{r})$

$$v(\boldsymbol{q}) = -4 \pi U \frac{\sin q \, r_\mathrm{s} - q \, r_\mathrm{s} \cos q \, r_\mathrm{s}}{q^3}, \tag{6}$$

and $\varepsilon(\boldsymbol{q})$ is the dielectric constant in the random phase approximation.

$$\varepsilon(\boldsymbol{q}) = 1 + \frac{4 \, e^2 \, m \, k_\mathrm{F}}{\pi \, h^2 \, q^2} \left[\frac{1}{2} + \frac{k_\mathrm{F}}{2 \, q} \left(1 - \frac{q^2}{4 \, k_\mathrm{F}^2} \right) \ln \left| \frac{q + 2 \, k_\mathrm{F}}{q - 2 \, k_\mathrm{F}} \right| \right], \tag{7}$$

where k_F is the Fermi wave vector. If it is assumed that the Fermi surface is spherical (i.e. neglecting the neck electrons in the noble metal alloys) the resistivity can be calculated from [16]

$$\varrho_0 = \frac{c \, (1 - c) \, m^2}{4 \, \pi \, h^3 \, k_\mathrm{F}^3} \int\limits_0^{2 \, k_\mathrm{F}} |v(\boldsymbol{q})|^2 \, q^3 \, \mathrm{d}q , \tag{8}$$

where c is the concentration of Au atoms.

The volume derivative of (8) is easily shown to be

$$\frac{\mathrm{d} \ln \varrho_0}{\mathrm{d} \ln V} = -5 \frac{\mathrm{d} \ln k_\mathrm{F}}{\mathrm{d} \ln V} - 2 \frac{\int\limits_0^2 \mathrm{d}x \, \dfrac{(\sin \alpha \, x - \alpha \, x \, \cos \alpha \, x)^2}{x^3 \, \varepsilon^2(x)} \dfrac{\mathrm{d} \ln \varepsilon(x)}{\mathrm{d} \ln V}}{\int\limits_0^2 \mathrm{d}x \, \dfrac{(\sin \alpha \, x - \alpha \, x \, \cos \alpha \, x)^2}{x^3 \, \varepsilon^2(x)}}, \tag{9}$$

where $x \equiv q/k_\mathrm{F}$, $\alpha \equiv k_\mathrm{F} \, r_\mathrm{s}$,

$$\frac{\mathrm{d} \ln \varepsilon(x)}{\mathrm{d} \ln V} = \frac{1}{3} \left[1 + \frac{\pi \, h^2 \, k_\mathrm{F}}{2 \, m \, e^2} \left(\frac{x^2}{1 + \dfrac{(1 - x^2/4)}{x} \ln \left| \dfrac{1 + x/2}{1 - x/2} \right|} \right) \right]^{-1}, \tag{10}$$

and U is assumed to be independent of volume and concentration. In the free electron approximation $\mathrm{d} \ln k_\mathrm{F}/\mathrm{d} \ln V = -1/3$. The integrals can be evaluated numerically if k_F and r_s are known; for both Ag and Au $k_\mathrm{F} = 1.20 \, \text{Å}^{-1}$ and $r_\mathrm{s} = 1.59 \, \text{Å}$ [18]. Evaluating the integrals yield $\mathrm{d} \ln \varrho_0/\mathrm{d} \ln V = 1.38$ for all Ag–Au alloys. As seen in Table 1 this is in general agreement with the experimental values; however, this model does not predict the concentration dependence. A similar calculation using this model was made for the Cu–Ag and Cu–Au alloys; in these cases the model predicted both the wrong sign and magnitude (in the case of the pseudopotential calculations [15] agreement between theory and experiment was obtained for the Cu–Ag alloys, but not the Ag–Au alloys).

These discrepancies in the theoretical prediction (from both models) are not too surprising because the effect of the low lying filled d-bands on the scattering potential was not explicitly considered. It is well known that the filled d-bands in the noble metals strongly interact with the conduction electrons in certain directions [1, 17]. From optical measurements [19] it has been shown that the d-levels of Cu and Ag do not overlap and form separate d-states in the alloys,

while for Au and Ag and for Au and Cu the d-levels overlap and form a common d-band in the alloys. These d-band effects on the scattering potential could account for the observed differences in the sign of the volume derivative of the resistivity for these alloy systems. In this light the good agreement between experiment and the square well potential model for the Ag–Au alloys is somewhat accidental since the d-band effects were not explicitly introduced into the scattering potential. Also this square well potential model does not account for the observed concentration dependence of $d \ln \varrho_0/d \ln V$ in the Ag–Au alloys. The observed concentration dependence of $d \ln \varrho_0/d \ln V$ could be a reflection of the d-band changing the form of the scattering potential with concentration. It would be interesting to compare the concentration dependence of $d \ln \varrho_0/d \ln V$ for alloys which form separate non-overlapping d-bands such as the Cu–Ag system with that of the Ag–Au alloys. (Unfortunately Cu and Ag are not very soluble.) In summary it appears that very explicit scattering potentials incorporating subtle d-bands effects will be necessary to account for the observed behavior of $d \ln \varrho_0/d \ln V$ in the noble metal–noble metal alloys.

4.2 Temperature dependence

The weak temperature dependence of $\varrho^{-1} d\varrho/dP$ for the alloys as compared to the strong temperature dependence of $\varrho_i^{-1} d\varrho_i/dP$ for Ag and Au suggests that disorder scattering has a dominating effect on the behavior of $\varrho^{-1} d\varrho/dP$ for the alloys. This can be seen in a more quantitative way by the following simple calculation. The temperature dependence of the sum of the first two terms in (3) is calculated and compared to the observed temperature dependence of $\varrho^{-1} d\varrho/dP$.

The values for $\varrho_i^{-1} d\varrho_i/dP$ at various temperatures were obtained from Goree and Scott's [2] data on pure Ag. The temperature dependence of ϱ_i was obtained from measurements on pure Ag, and ϱ, ϱ_0 and $\varrho_0^{-1} d\varrho_0/dP$ were obtained from the experimental data on the alloys. Constant volume corrections should be made on ϱ and ϱ_i, however, this amounted to only 1.5% at 300 °K and was neglected. In Fig. 5 the calculated sum of the first two terms of (3) and the experimental temperature dependence of $\varrho^{-1} d\varrho/dP$ are compared for the $c = 0.25$ alloy. Similar results were also obtained for the $c = 0.50$ and 0.75 alloys. It is observed that the calculated curve reflects the general temperature dependence of the experimental curve. The coefficients ϱ_0/ϱ and ϱ_i/ϱ determined the relative effect of the two scattering mechanisms on $\varrho^{-1} d\varrho/dP$. Typically at high temperatures $\varrho_0/\varrho \approx 3.5 \varrho_i/\varrho$ and at low temperatures where $\varrho_i^{-1} d\varrho_i/dP$ is large, negative and temperature dependent $\varrho_0/\varrho \gg \varrho_i/\varrho$. The sign, the magnitude and the weak temperature dependence of $\varrho^{-1} d\varrho/dP$ is a result of the dominating influence of the disorder scattering.
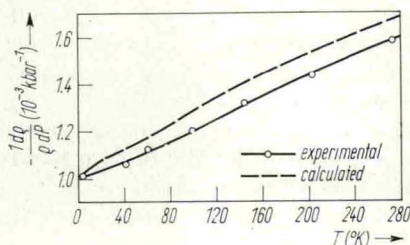

Fig. 5. A comparison of the temperature dependence of the measured and calculated pressure derivative of the resistivity for the 25 at% Au–75 at% Ag alloy