that d ln ϱ_0/d ln V is positive, concentration dependent and attains a maximum value of 1.38 for the $c = 0.5$ alloy. It should be noted that there may be a slight error in d ln ϱ_0/d ln V for the concentrated alloys because the compressibility of these alloys was obtained by a linear extrapolation between the values for pure Ag and Au. Bridgman [5, 6] has observed a slight deviation from linearity in the concentration dependence of the compressibility of these alloys at $T = 300\ °K$. If this deviation persists to low temperatures, then d ln ϱ_0/d ln V would be slightly enhanced for the $c = 0.25$ and 0.5 alloys.

4. Discussion

According to Matthiessen's rule for binary alloys the lattice resistivity and the residual resistivity are additive. This implies that the scattering of conduction electrons by phonons and impurities are independent and a single relaxation time can describe each type of scattering process. However, deviations from Matthiessen's rule can occur for a number of reasons [8, 9]. Some of the more important effects are listed as follows: 1. the phonon spectrum can change upon alloying, 2. the Fermi surface or electronic structure changes upon alloying, and 3. the relaxation times for different scattering mechanisms can have different anisotropies. The deviation from Matthiessen's rule, $\varDelta$, is defined as follows

$$\varrho = \varrho_1 + \varrho_0 + \varDelta , \qquad (2)$$

where ϱ is the resistivity of the alloy measured at T, ϱ_1 is the lattice resistivity of the host metal measured at T, and ϱ_0 is the residual resistivity of the alloy. The pressure derivative of the resistivity for an alloy will then have three terms [1]

$$\frac{1}{\varrho}\frac{d\varrho}{dP} = \frac{\varrho_1}{\varrho}\left(\frac{1}{\varrho_1}\frac{d\varrho_1}{dP}\right) + \frac{\varrho_0}{\varrho}\left(\frac{1}{\varrho_0}\frac{d\varrho_0}{dP}\right) + \frac{\varDelta}{\varrho}\left(\frac{1}{\varDelta}\frac{d\varDelta}{dP}\right). \qquad (3)$$

In the case of the concentrated $Ag_{1-c}Au_c$ alloys studied here it is expected that deviations from Matthiessen's rule could occur for all of the above reasons. In the noble metals there are two groups of conduction electrons, the neck electrons and the belly electrons. Dugdale and Basinski [8] have shown the difference in anisotropics of the relaxation times between the neck and belly electrons to be the primary cause for deviations from Matthiessen's rule in dilute Ag–Au alloys. (Hereinafter, the underline notation, X–Y, will imply a dilute alloy with X as the solvent.)

From (3) it can be seen that the pressure derivative of the residual resistivity can be obtained by measuring the pressure derivative of the resistivity at low temperatures. The lattice term goes to zero as T approaches zero, since ϱ_1/ϱ goes to zero and $\varrho_1^{-1}\,d\varrho_1/dP$ remains finite [2]. On the basis of Dugdale and Basinski's model it can be shown that $\varDelta^{-1}\,d\varDelta/dP$ remains finite and $\varDelta/\varrho$ goes to zero as T goes to zero. In the $Ag_{1-c}Au_c$ alloys the resistivity is independent of temperature up to $10\ °K$, and there should be little error in equating $\varrho_0^{-1}\,d\varrho_0/dP$ to the measured pressure derivative of the resistivity at $4\ °K$.

4.1 Residual resistivity

Lennsen and Michels [10] have shown by using Nordheim's [11] form for chemical impurity scattering that the volume derivative of the residual resistivity is $-1/3$. This result is based on the free electron approximation and that

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the scattering potential is independent of volume. As can be seen by the variety of values for d ln ϱ_0/d ln V for the noble metal–noble metal alloys [3], this model is too simple.

The Fermi surface of the noble metals consists of a spherical belly and necks which contact the [111] zone faces. If it is assumed that the conduction electrons can be represented by a two-band model [8] (the conductivities of the individual carriers are additive), then the volume derivative of the residual resistivity can be expressed as follows

$$\frac{\mathrm{d}\ln\varrho_0}{\mathrm{d}\ln V} = \frac{\varrho_0}{\varrho_0^{\mathrm{B}}}\left(\frac{\mathrm{d}\ln\varrho_0^{\mathrm{B}}}{\mathrm{d}\ln V}\right) + \frac{\varrho_0}{\varrho_0^{\mathrm{N}}}\left(\frac{\mathrm{d}\ln\varrho_0^{\mathrm{N}}}{\mathrm{d}\ln V}\right), \tag{4}$$

where the superscripts B and N refer to the belly and neck electrons, respectively. From Dugdale and Basinski's [8] estimate of the ratio of the neck conductivity to the belly conductivity for impurity scattering in dilute Ag–Au alloys, $\varrho_0/\varrho_0^{\mathrm{B}}$ and $\varrho_0/\varrho_0^{\mathrm{N}}$ were calculated to be 0.75 and 0.25, respectively. Thus, the belly term is more heavily weighted than the neck term; however, this does not necessarily mean that effect of the neck electrons can be neglected without further justification. Ziman [14] has argued that in the case of uncharged impurities the perturbation due to the impurities is confined to the immediate vicinity of each impurity atom. Since the neck electrons move in between the atoms, this implies the belly electrons are predominantly scattered and the relaxation time for the neck electrons is greater than the relaxation time for the belly electrons. (For strongly charged impurities the scattering tends to be more isotropic.) Thus the neck electron term in (4) can be neglected to a first approximation.

The cross-sectional area of the bellies for Ag and Au are of nearly the same size, while in the case of Cu the cross-sectional area of the belly is about 25% larger. The cross-sectional area of the belly for Au, however, is less sensitive to pressure than in the case of Cu and Ag [12, 13]. Since d ln ϱ_0/dV was nearly the same value for both the dilute Ag–Cu and Au–Cu alloys, it appears that the effect of pressure on the belly areas does not have a significant effect in determining the differences in the sign and magnitudes of d ln ϱ_0/d ln V in the noble metal–noble metal alloys.

In any theoretical calculation of d ln ϱ_0/d ln V for these alloys the use of a spherical Fermi surface is probably a good approximation. Du Charme and Edwards [15] have shown on the basis of a pseudo-potential formulation that the form of the effective scattering potential is an important factor for accurately predicting the volume derivative of the residual resistivity in dilute noble metal alloys containing monovalent and higher-valent impurities. In the case of the dilute Cu–Ag and Ag–Cu alloys good agreement between theory and experiment was found, however, for the dilute Ag–Au and Au–Ag alloys the theory predicted the wrong sign.

Recently Haga [16] has calculated (using a screened square well impurity potential model) the nuclear specific heat and other phenomena related to nuclear magnetic resonance experiments for concentrated Ag–Au alloys. He obtained good agreement between theory and experiment. In this model it is assumed that the unscreened impurity potential has the form: $v_0(r) = -U$ for $r < r_{\mathrm{s}}$ and $v_0(r) = 0$ for $r > r_{\mathrm{s}}$, where r_{s} is the radius of an atomic cell. The