mated uncertainties of the measurements. We have confined the comparison of our data to the most recent published work as it is recognized that much of the disagreement with earlier studies was due to the nonhydrostatic pressure techniques employed. This problem has been discussed elsewhere.[13,22]

Finally, we find no indication of any change in the initial phase of the dHvA oscillations associated with the minimum cross-sectional area of the hole surface.

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Pseudopotential Determination of Volume Dependence of Residual Resistivity in Binary Alloys*

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Ashcroft pseudopotential form factors are used to predict the volume dependence of residual resistivity in dilute noble-metal alloys. A trend toward negative-volume derivatives for lower-valence impurities is found for all solvents. Reasonable agreement with experimental magnitudes of the volume derivative are noted for many combinations.

I. INTRODUCTION

Since the introduction of solid and fluid helium as pressure-transmitting media, reliable measurements of the volume dependence of the residual resistivity ρ_0 of alloys have been obtained. Dugdale[1] has measured the volume derivatives of the residual resistivity of noble-metal alloys containing monovalent and multivalent impurities. In the case of impurities with valences of 3, 4, and 5, $d\ln\rho_0/d\ln V$

was found to be consistently positive, while for monovalent and divalent impurities, $d\ln\rho_0/d\ln V$ was found to be both positive and negative.

On the basis of a simple free-electron model, where the screening of the impurity potential is calculated by the Thomas-Fermi method,[1] the value of $d\ln\rho_0/d\ln V$ was found to be between $+\frac{1}{3}$ and $+1$. This simple model cannot predict negative-volume derivatives or magnitude variations when the impurity is varied and is not applicable to the case of monovalent substitutions. As Ziman[2] has pointed out, the already well-known need for detailed form factors to calculate resistivity should also be found in investigations of its volume derivative.

Reasonable form factors are now available based on the Ashcroft[3] one-parameter pseudopotential. This parameter, the core radius, can be determined from Fermi-surface studies and liquid-resistivity experiments. We find that this simple improvement in effective scattering potential allows prediction of observed trends. It thereby provides an initial approach to the study of physical conditions which contribute to the sign and magnitude of the volume derivative of the resistivity.

II. LOCAL PSEUDOPOTENTIAL FORMULATION OF RESIDUAL RESISTIVITY

Harrison[4] has taken the simple Mott and Jones[5] expression for the dc conductivity and recast it in terms of the pseudopotential concept. The conduction electrons now scatter effectively from impurity atoms via a weak pseudopotential. To a first-order perturbation treatment, he found that the resistivity of a dilute binary alloy has the form

$$\rho_0=\frac{c3\pi m\Omega_0}{8\hbar e^2E_F}\int_0^2[\Delta w(x)]^2x^3\,dx, \tag{2.1}$$

where c is the atomic concentration of impurity, Ω_0 is the atomic volume of the host, and $x=q/k_F$. The term $\Delta w(x)$ represents the difference in pseudopotential form-factor characteristic of the solute and solvent. This treatment assumes a random substitution of the impurity and sphericity in the integral over the Fermi surface. Ziman[6] indicates that this free-electron aspect is a reasonable assumption, at least in the case of low-valence substitutions, when belly orbits prevail as contributors to the impurity resistivity for the noble-metal alloys.

The Ashcroft pseudopotential form factor for either the host or impurity may be written[7] as

$$w(x)=\frac{-4e^2k_F}{3\pi}\frac{Z}{Z_0}\frac{\cos(Rk_Fx)}{x^2\epsilon_0(x)}, \tag{2.2}$$

where k_F, Z_0, and $\epsilon_0(x)$ are the Fermi wave number, the valence, and dielectric function appropriate to the host metal. R and Z are the core radius and valence characteristic of the type atom considered. With this choice of form factor, Eq. (2.1) may be expressed in the more convenient form of

$$\rho_0=\frac{c4m^2e^2\Omega_0}{3\pi\hbar^3}\int_0^2\frac{dx}{x\epsilon_0^2(x)}\left[\frac{Z_i}{Z_0}\cos(R_ik_Fx)-\cos(R_0k_Fx)\right]^2. \tag{2.3}$$

The Hartree dielectric function $\epsilon_0(x)$, which accounts for electron-electron interactions within the framework of a local pseudopotential, has the well-known dependence on the Fermi wave number

$$\epsilon_0(x)=1+\frac{2me^2}{\pi k_F\hbar^2x^2}\left(\frac{(1-\frac{1}{4}x^2)}{x}\ln\left|\frac{1+\frac{1}{2}x}{1-\frac{1}{2}x}\right|+1\right). \tag{2.4}$$

Volume dependence of the resistivity within this simple formulation enters in three ways: in the coefficient of (2.3), in the argument of the cosines, and in the dielectric screening. We assume that as the volume is reduced, the Fermi wave number increases according to the free-electron assumption of

$$k_F=(3\pi^2Z_0/\Omega_0)^{1/3}. \tag{2.5}$$

III. RESULTS

Equation (2.3) was integrated numerically to calculate the magnitude of the residual resistivity for various valence solutes in copper, silver, and gold. The results are summarized in Table I, where they are compared to experimental values obtained by Linde.[8] His experiments were not performed at low temperatures and therefore may have some inaccuracy due to deviations from Mathiessen's rule as noted by Dugdale and Basinski.[9]

The core radii used in most cases were obtained from the best fit to available experimental points furnished by dHvA or optical data on pure metals

TABLE I. Calculated (observed)[a] residual resistivities of binary noble-metal alloys in $\mu\Omega$ cm/at.%.

Solute (Core radius Å)	Valence	Solvent Cu	Ag	Au
Cu(0.430)	1		0.09(0.077)	(0.45)
Ag(0.550)	1	0.10(0.14)		0.09(0.36)
Au(0.430)	1	(0.55)	0.09(0.36)	
Zn(0.683)	2	0.64(0.32)	0.41(0.64)	0.50(0.95)
Cd(0.744)	2	1.13(0.30)	0.52(0.38)	0.82(0.63)
Hg(0.484)	2	0.61(1.0)	1.58(0.79)	1.02(0.44)
Al(0.610)	3	1.35(1.25)	2.67(1.95)	2.15(1.87)
Ga(0.535)	3	1.96(1.42)	4.25(2.36)	3.35(2.2)
In (0.590)	3	1.44(1.06)	3.03(1.78)	2.41(1.39)
Ge(0.506)	4	5.66(3.79)	11.0(5.5)	22.4(5.2)
Sn(0.686)	4	3.0 (2.88)	4.21(4.36)	3.89(3.36)

[a]From thesis by J. O. Linde (unpublished); given by F. J. Blatt, in *Solid State Physics*, edited by F. Seitz and and D. Turnbull (Academic, New York, 1957), p. 318.

as reported by Fukai.[7] Exceptions to these were the core radii used for Cu, Ag, Au, and Sn which were obtained from investigations by Ashcroft and Langreth[10] of liquid-metal properties. The sensitivity of the formulation to differences in core radii prevented analysis of the Cu-Au systems.

The calculated values generally compare well with reported magnitudes. Agreement with experimental trends are evident, involving variation of host for a given impurity or change of solute in a given solvent. Less agreement is noted in some cases involving Cd, Zn, and Au. Calculated magnitudes also tend to be higher than observed values for higher-valence impurities.

The volume dependence of the residual resistivity was also determined by using Eq. (2.3) to calculate ρ_0 at reduced volumes. The values obtained for 1% volume reduction are summarized in Table II and compared, when possible, to experimental results found by Dugdale.[1]

We find a trend towards negative-volume derivatives for low-Z impurities not unlike Dugdale. Wrong signs are predicted only for the Zn-Cu, Au-Ag, and Cd-Ag systems. An agreement in magnitude and its variation with solute is especially noticeable for valence-3 and -4 impurities in Ag.

The sign of the volume derivative generally did not change for a given model system as it was reduced to one-half its original volume. Exceptions occurred for Al, In, and Sn in Cu, Zn, and Sn in Ag, and Sn in Au. Their behavior is exemplified by the volume dependence of the residual resistivity of Zn in Ag shown in Fig. 1. The sign change found in the volume derivative is similar to the volume dependence observed[11] for the lattice resistivity in some pure alkali metals.

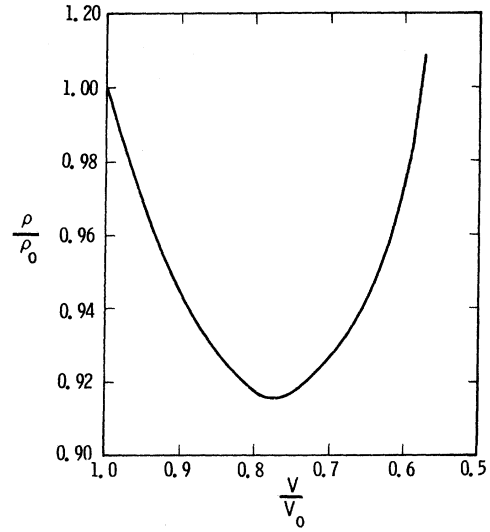

FIG. 1. Calculated reduced resistivity as a function of reduced volume for the dilute Zn-Ag alloy.

TABLE II. Calculated (observed)[a] volume derivatives of residual resistivity $d\ln\rho_0/d\ln V$ due to impurities in the noble metals.

Impurity	Valence	Solvent Cu	Ag	Au
Cu	1		−0.3(−0.4)	
Ag	1	−0.2(−0.6)		−0.3 (1.2)
Au	1		−0.3 (1.0)	
Zn	2	−0.8 (0.3)	0.7 (0.9)	−0.4(−0.9)
Cd	2	−0.8(−0.3)	−0.5 (1.0)	−0.9
Hg	2	1.5	1.1 (1.7)	1.3
Al	3	1.0	1.5	1.5
Ga	3	1.5 (0.9)	1.3 (1.1)	1.4 (1.1)
In	3	1.2 (0.7)	1.5 (1.6)	1.5 (0.1)
Ge	4	1.4 (0.6)	1.2 (0.8)	0.8 (0.8)
Sn	4	0.2 (0.9)	1.3 (1.0)	1.2 (1.4)

[a] J. S. Dugdale, in *Physics of Solids at High Pressures*, edited by C. T. Tomizuka and R. M. Emrich (Academic, New York, 1965), p. 16.

IV. COMMENTS AND CONCLUSIONS

The results of Table I imply that we have made a reasonable choice of pseudopotential form factor to study residual resistivity in binary alloys. The one-parameter point-ion model was used previously by Harrison[4] to study the resistivity of copper alloys. It did not reflect any better conformity with observed data, even though he adjusted the parameter to optimize such agreement with experiment.

Table II demonstrates that our formulation involving the Ashcroft form factor has close to the correct volume dependence. In order to detail this behavior, we take the logarithmic volume derivative of Eq. (2.3):

$$\frac{d\ln\rho_0}{d\ln V}=\frac{d\ln\Omega_0}{d\ln V}+d\ln\left(\int_0^2\frac{J(x)\,dx}{x\epsilon_0^2(x)}\right)\,d\ln V\ , \tag{4.1}$$

where

$$J(x)=[(Z_i/Z_o)\cos(R_i k_F x)-\cos(R_0 k_F x)]^2. \tag{4.2}$$

Equation (4.1) may be separated into more meaningful terms by defining

$$I_1=-2\int_0^2\frac{dx\,J(x)}{x\epsilon_0^2(x)}\frac{d\ln\epsilon_0(x)}{d\ln V}\Big/\int_0^2\frac{J(x)\,dx}{x\epsilon_0^2(x)} \tag{4.3}$$

and

$$I_2=\int_0^2\frac{dx\,J(x)}{x\epsilon_0^2(x)}\frac{d\ln J(x)}{d\ln V}\Big/\int_0^2\frac{J(x)\,dx}{x\epsilon_0^2(x)}\ . \tag{4.4}$$

Combining these definitions with the obvious proportionality of the total volume to Ω_0, we find

$$\frac{d\ln\rho_0}{d\ln V}=1+I_1+I_2. \tag{4.5}$$

The term I_1 isolates the volume dependence of the dielectric function. We observed it always to be negative in sign but less than 1 in magnitude. The second integral I_2 involves the volume dependence of Eq. (4.2). It was found to take on both positive and negative values as a function of Z_i, k_F and the core radii. For low-valence impurities, I_2 was negative enough to make $d\ln\rho_0/d\ln V$ negative.

The term I_2 was often very sensitive to the choice of impurity core radius. The core radius $R_i = 0.59$ Å used for In, which was derived[7] from dHvA data of O'Sullivan, Schirber, and Anderson,[12] gives reasonable agreement with the experimental sign and magnitude of $d\ln\rho_0/d\ln V$ for In in Cu. The value $R_i = 0.70$ Å suggested by Ashcroft[10] produces the wrong sign. The Ashcroft radius also gives poor agreement with the experimental residual resistivity value for this alloy. In the case of zinc, however, a change of core radius from $R_i = 0.683$ Å to 0.673 Å doubled the magnitude of the volume derivative but varied the predicted residual resistivity of Zn in Ag by only 2%. More experimental data combined with a more complex formulation may allow the volume derivative to be used as a critical determiner of pseudopotential parameters.

The use of local pseudopotentials is certainly questionable for Zn,[13] Cd,[14] and the noble metals.[4,15] The results of Table II indicate, however, that this approximation is only poor enough to predict the wrong sign for the volume derivative when both form factors involved are strongly nonlocal. A correction for this effect in I_2 as well as proper inclusion of correlation and exchange in I_1 may be sufficient to allow prediction of the correct sign for all low-valence impurity systems.

The assumption of Fermi-surface sphericity made in our integrations should be worse for high-valence impurity systems according to a rough calculation by Ziman.[6] Overestimation of belly contributors should give lower resistivities than those we predict in Table I. Evidently, the form of the effective scattering potential is the most important factor for the accurate prediction of volume derivatives of the residual resistivity.

In conclusion, we note that a simple one-parameter pseudopotential can predict much of the correct volume dependence of the residual resistivity observed in the noble-metal alloys. Experiments are badly needed on simpler (from a theoretical point of view) systems so that the assumptions involved in our crude model can be better isolated and their relative influence thereby determined.

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