last integral. Then, setting $t=rx/(\pi\xi_0)$, we have

$$I=\frac{k_F}{\pi^2 r}\frac{1}{hv_0}\sin k_F r\left[K_0\left(\frac{r}{\pi\xi_0}\right)-\int_{ar/\pi\xi_0}^{\infty}\frac{\cos t}{t}dt\right]. \quad \text{(D11)}$$

Asymptotically

$$-\int_{x}^{\infty}\frac{\cos t}{t}dt\sim\frac{\sin x}{x}, \quad x\gg 1, \quad \text{(D12)}$$

while $K_0(x)$ falls off exponentially. Thus the asymptotic behavior of $P_A(r)$ is given by

$$P_A(r)\sim\frac{9n\epsilon_0^2(0)}{2(\hbar\omega)^2}\frac{\sin^2 k_F r\,\sin^2\left(\frac{\epsilon_0}{\hbar\omega}\frac{r}{\pi\xi_0}\right)}{(k_F r)^4}. \quad \text{(D13)}$$

Since $a=h\omega/\epsilon_0\gg 1$, the range of correlation is determined by the K_0 function which drops off rapidly when $r/(\pi\xi_0)\gtrsim 1$. Thus correlation distance is the order of $\pi\xi_0\simeq 10^{-4}$ cm.

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Residual Resistivity of Gold Alloys: Dependence on Periodic Table*

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The residual resistivities of dilute alloys of gold are calculated by the same method which was employed in a similar study of the residual resistivities of copper and silver alloys. As in the earlier work, the calculated results agree well with experiment with the exception of the alloys gold-copper and gold-silver. The application of the modification of the Friedel sum condition to other problems is suggested.

I. INTRODUCTION

In a previous paper[1] attention was directed to the fact that the residual resistivities of dilute noble metal alloys exhibited a very systematic dependence on the position which the solute occupies in the periodic table of the elements. The most pronounced dependence is on the valence of the solute: $\Delta\rho$, the residual resistivity per atomic percent solute, increases approximately as the square of the valence difference Z. Since we are concerned here with monovalent solvent metals, we have $Z=Z'-1$ where Z' is the valence of the solute. In addition to this well-known Z^2 dependence, for which Mott[2] and Friedel[3] have provided satisfactory explanations, $\Delta\rho$, for a given Z, also depends systematically on the row, or period, of the periodic table to which the solute belongs. Solutes which occupy the silver row of the periodic table invariably give rise to smaller values of $\Delta\rho$ in every one of the noble metals than do solutes which belong to the copper row. In the notation of I, we can express this experimental observation by the following inequalities

$$\frac{\mathrm{Cu(Cu)}}{\mathrm{Cu(Ag)}}>1;\quad \frac{\mathrm{Ag(Cu)}}{\mathrm{Ag(Ag)}}>1;\quad \frac{\mathrm{Au(Cu)}}{\mathrm{Au(Ag)}}>1.$$

Calculations of $\Delta\rho$ based on a free electron model, such as those of Mott, Friedel and others[4,5] differ in their numerical results but do all lead to the conclusion

$$\frac{\mathrm{Cu(Cu)}}{\mathrm{Cu(Ag)}}=\frac{\mathrm{Ag(Cu)}}{\mathrm{Ag(Ag)}}=\frac{\mathrm{Au(Cu)}}{\mathrm{Au(Ag)}}=1.$$

Calculations of the residual resistivities of dilute alloys of copper and silver where found to be in good agreement with experimental results if the expansion of the lattice in the neighborhood of a solute atom was taken into account in a manner suggested by Harrison.[6] In the present article we report results of similar calculations on dilute alloys of gold.

II. CALCULATION AND RESULTS

It was shown in I that the discrepancy between the observed values of the ratios Cu(Cu)/Cu(Ag) and Ag(Cu)/Ag(Ag) and those calculated in a free electron approximation could be obviated by a suitable modification of the Friedel sum condition.[3] The Friedel sum rule states that

$$(2/\pi)\textstyle\sum_l(2l+1)\delta_l=N, \quad (1)$$

where δ_l are the phase shifts evaluated for electrons at the Fermi surface and N is the excess charge,

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[1] F. J. Blatt, Phys. Rev. 108, 285 (1957). Hereafter, we shall refer to this paper as I.

[2] N. F. Mott, Proc. Cambridge Phil. Soc. 32, 281 (1936).

[3] J. Friedel, *Advances in Physics* (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 446.

[4] F. J. Blatt, Phys. Rev. 99, 1708 (1955).

[5] P. de Faget de Casteljau and J. Friedel, J. phys. radium 17, 27 (1956).

[6] W. A. Harrison (to be published).

introduced into the lattice by the solute, which must be screened by a readjustment of the free electrons. As in I, we shall set

$$N = Z - \delta V/\Omega, \tag{2}$$

where $\delta V/\Omega$ is the fractional change in size of the cell occupied by the solute atom. This choice of N reflects formally the partial screening accomplished by displacement of the lattice ions in the immediate neighborhood of the solute. The quantity $\delta V/\Omega$ may be determined from experimental results on the change in average lattice parameter due to alloying. The relation is

$$\frac{\delta V}{\Omega} = \frac{3}{\gamma}\left(\frac{\delta a}{a}\right), \tag{3}$$

TABLE I. Lattice expansion of gold due to alloying.[a]

Solute	Z	$\delta a/a$	$\delta V/\Omega$	N
Cu	0	−0.085	−0.2082	0.2082
Zn	1	−0.04	−0.098	1.098
Ga	2	−0.018	−0.0441	2.0441
Ge	3	+0.02	+0.049	2.951
As	4	···	+0.135[b]	3.865
Ag	0	−0.002	−0.005	0.005
Cd	1	+0.04	+0.098	0.902
In	2	+0.068	+0.1665	1.8335
Sn	3	+0.1	+0.245	2.755
Sb	4	+0.125	+0.306	3.694

[a] Values of $\delta a/a$ are taken from G. V. Raynor, in *Progress in Metal Physics* (Interscience Publishers, Inc., New York, 1949), Vol. 1, p. 1.
[b] Extrapolated result.

TABLE II. Phase shifts and the Friedel sum for impurities in gold.

Solute	kr'	$\alpha r'$	δ_0	δ_1	δ_2	δ_3	$\frac{2}{\pi}\Sigma \times(2l+1)\delta_l$	N
Cu	1.7763	1.92	0.1695	0.0449	0.0043	0.0002	0.2082	0.2082
Zn	1.8551	2.42	0.6931	0.2913	0.0271	0.0015	1.091	1.098
Ga	1.8914	2.763	0.9844	0.6428	0.0568	0.0029	2.048	2.0441
Ge	1.9509	3.025	1.115	1.001	0.0974	0.0050	2.954	2.951
As	2.0028	3.275	1.221	1.341	0.1612	0.0079	3.887	3.865
Ag	1.9168	1.9202	0.0039	0.0012	0.0001	···	0.005	0.005
Cd	1.9807	2.421	0.5379	0.2430	0.0277	0.0017	0.9023	0.902
In	2.0211	2.765	0.8391	0.5669	0.0635	0.0039	1.8364	1.8335
Sn	2.0655	3.03	0.9998	0.9061	0.1097	0.0065	2.745	2.755
Sb	2.0988	3.275	1.130	1.239	0.1777	0.0098	3.693	3.694

where $(\delta a/a)$ is the relative change in lattice parameter in percent per atomic percent of solute, and $\gamma = 3(1-\sigma)/(1+\sigma)$, σ being Poisson's ratio.

The potentials which were used in this calculation were square wells whose radii are given by

$$r' = r_s[1+\delta V/\Omega]^{\frac{1}{3}}, \tag{4}$$

where r_s is the radius of the equivalent sphere, $r_s = (3/4\pi)\Omega^{\frac{1}{3}}$. The depths of the potential wells were adjusted until the phase shifts satisfied Eq. (1), with N given by Eq. (2). The pertinent information for the gold alloys is given in Table I. The calculated phase shifts are listed in Table II. The calculated and experimental results are shown in Table III.

TABLE III. Residual resistivities of dilute gold alloys. Numerical values are in μohm-cm/atomic percent solute.

			Other calculated results							
Solute	Present calc	Exp.[a] result	Fu I[b]	Fu II[b]	Fu III[b]	Fu IV[b]	B[c]	F[d]	F,F[e]	R[f]
Cu	0.080	0.48								0.52
Zn	1.239	0.96	2.01	3.09	0.75	1.45		0.9	1.35	0.35
Ga	3.117	2.2					3.0	2.7	2.7	
Ge	5.415	5.2					5.6	5.4	5.3	
As	7.633	8.0					9.2	9.0	8.1	
Ag	0.000	0.38								0.41
Cd	0.756	0.64	2.01	3.09	0.75	1.45		0.9	1.35	0.38
In	2.333	1.41					3.0	2.7	2.7	
Sn	4.521	3.63					5.6	5.4	5.3	
Sb	6.890	6.8					9.2	9.0	8.1	

[a] J. O. Linde, Ann. Physik **15**, 219 (1932).
[b] H. Fujiwara, J. Phys. Soc. Japan **11**, 376 (1956).
[c] See reference 4.
[d] See reference 3.
[e] See reference 5.
[f] See reference 7.

DISCUSSION

In Fig. 1 we show the experimental and calculated values of $\Delta\rho$ plotted against Z^2. With the exception of the calculated resistivities for gold-copper and gold-silver alloys, the results agree reasonably well with the observed residual resistivities. It is obvious from Fig. 1 that the numerical results differ from the observed resistivities by significant amounts, especially for $Z=2$. Still, the discrepancies are no more than in previous calculations[2–5] as can be seen by examination of Table III. At the same time, the dependence of $\Delta\rho$ on the row of the periodic table which the solute occupies is reflected in the calculated values. The dependence on the row of the periodic table is exhibited most effectively in Fig. 2 where the ratios Au(Cu)/Au(Ag) are shown. If the influence of lattice strain had been neglected, the calculated values of these ratios would all be unity.

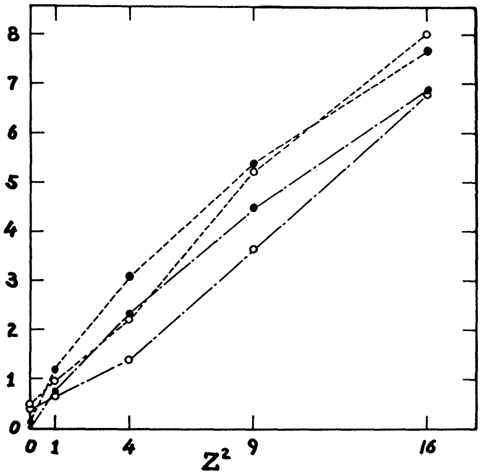

FIG. 1. The residual resistivities of dilute alloys of gold in μohm-cm/atomic % solute as functions of the square of the valence difference between solute and solvent atoms. The dotted lines connect experimental (○) and calculated (●) points of the Au(Cu) series; the dot-dash lines connect experimental (○) and calculated (●) points of the Au(Ag) series.

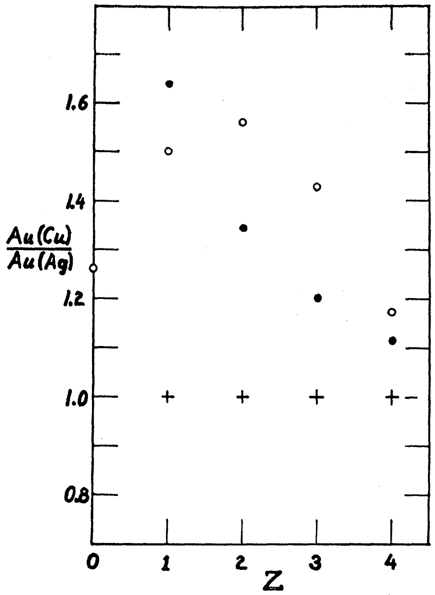

FIG. 2. The ratios of the residual resistivities of the Au(Cu) series of alloys to the residual resistivities of the Au(Ag) series of alloys plotted against Z, the valence difference between solute and solvent atoms. The experimental and calculated points are indicated by circles (○) and dots (●), respectively. The crosses (+) show the ratios (unity) that would have been obtained if the Friedel condition had not been modified to account for lattice strain about the solute atoms.

A very serious discrepancy exists between the calculated and experimental values of $\Delta\rho$ for $Z=0$. The present calculation, of course, takes account only of valence difference and lattice strain. Perturbations which arise as a result of differences in the core potentials of the solvent and solute ions are completely neglected. In the work of Roth[7] these differences are taken into account specifically and in these alloys make the dominant contribution to $\Delta\rho$. Roth also calculated the effect of the strain field about a copper ion in solid solution in gold. The result, $\Delta\rho$ (strain field) $=0.07$ μohm-cm/atomic %, obtained by a method quite different from that presented here is in surprisingly good agreement with the value 0.08 μohm-cm/atomic percent of Table III. In the case of alloys of copper with silver and silver with copper, the results of Roth, uncorrected for strain scattering, are very much too small. Here the results of I are in good agreement with the experimental data, indicating that for these alloys scattering by the strain field is most important.

It would appear, then, that the influence of valence difference between solute and solvent and of lattice strain due to the solute can be taken into account by the modification of the Friedel condition employed in the present calculation and in I. In those cases where differences in the core potential are important the present method is, of course, completely inadequate. Such situations are most likely to arise when $Z=0$, because when $Z\neq 0$ scattering by the screened Coulomb field is probably the most important effect.

As was remarked in I, the influence of lattice strain which gives rise to a dependence of $\Delta\rho$ on the row of the periodic table occupied by the solute should also influence other properties of dilute alloy systems. The thermoelectric power of the noble metal alloys is now under investigation. Moreover, the modification of the Friedel rule may be important also in the interpretation of a variety of properties of dilute alloys other than those of charge transport, such as solute diffusion,[8] magnetic susceptibility,[9] electronic specific heat,[10] and the Knight shift.[11] The influence of lattice strain on these phenomena is currently being studied by using the model employed in this and the previous article.[1]

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