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Pseudo-Atom Phase Shifts for Monovalent Metals and Alloys. II. Monovalent Impurity Resistivities in Monovalent Metals*

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Impurity resistivities of monovalent ions in various monovalent matrices are evaluated for both solids and liquids. The comparison with experiment is satisfactory and lends general support to the pseudo-atom concept of Ziman and Harrison and the liquid-alloy resistivity theory of Faber and Ziman.

1. INTRODUCTION

In recent years, the concept of a pseudo-atom[1,2] has arisen in the theory of metals. Any given metal or alloy is to be viewed as a superposition of such pseudoatoms, each one having a field defined by that of the individual ion under study, screened by an electron gas of density equal to the average for the valence electrons in the actual matrix. The transport properties are then considered in two stages: (i) the scattering of free electrons from a single pseudo-atom and (ii) the interaction of the scattered waves from the various sites.

The solution of the problem posed by (i) is conveniently summarized by a set of partial-wave phase shifts appropriate to the Fermi level of the alloy. In terms of these, formulas for impurity resistivities in solids[1] and liquids[3] can be derived. Hitherto, analysis of such results has been inhibited by the lack of detailed knowledge of the phase shifts, but the recently derived data of Meyer *et al.*[4] for monovalent ions now enable numerical computations to be carried out for such ions in monovalent matrices. It is, perhaps, worth mentioning at this stage that, as Ziman[1] has pointed out, in an exact treatment it does not matter whether we consider pseudo-atom or pseudopotential scattering, for the corresponding wave functions have identical asymptotic forms, thus producing identical sets of phase shifts (modulo π) and, therefore [cf. (2) below] identical physical effects. To this extent, then, we can if necessary regard the one, even when calculated within an approximate framework, as a fair description of the other. Generally speaking [cf. (7) below] we think of the data of Meyer *et al.*[4] as pseudopotential phase shifts, but, perhaps in the case of vacancies, which will also be considered, the pseudoatom picture is more physically appealing, as there a whole screened ion is removed from the matrix.

The purpose of this paper is to present and discuss impurity resistivity calculations,[5,6] based on the data of Meyer *et al.*, with a view to testing the pseudo-atom concept of Ziman and Harrison and the liquid-alloy theory of Faber and Ziman (hereafter FZ).

The plan of the work is as follows. In Sec. 2, we introduce and discuss, in general terms, the impurity resistivity formula of Ziman's for solids, and in Sec. 3, a similar analysis for the FZ theory of liquids is made. In Sec. 4, the detailed phase-shift data are introduced and applied to the formalism of the two previous sections. Finally, in Sec. 5, there is a discussion.

2. SOLIDS

Here, the impurity resistivity per atomic percent of impurity 1 added to a pure metal 0 will be taken to be[7]

$$\rho_s=(\lambda/a_0k_F)\int_0^2 |f_1-f_0|^2\xi^3d\xi\,, \tag{1}$$

where

$$f_j(\xi)=(2i/3\pi)\sum_0^\infty(2l+1)(e^{2i\eta_l^j}-1)P_l(1-\tfrac{1}{2}\xi^2) \tag{2}$$

is the (reduced) scattering amplitude for a pseudo-atom j, the η_l^j being the various partial-wave phase shifts evaluated in both cases at the pure-metal Fermi level,

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[1] J. M. Ziman, Advan. Phys. **13**, 89 (1964).

[2] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

[3] T. E. Faber and J. M. Ziman, Phil. Mag. **11**, 153 (1965).

[4] A. Meyer, C. W. Nestor, Jr., and W. H. Young, Advan. Phys. (to be published).

[5] J. M. Dickey, A. Meyer, and W. H. Young, Phys. Rev. Letters **16**, 727 (1966).

[6] For a review of the work of Refs. 3 and 5, see T. E. Faber, Advan. Phys. (to be published).

[7] Reference 1, p. 129.

k_F. The constant λ, which will be used quite frequently below, is given by

$$\lambda = 9\pi^3\hbar a_0/1600e^2 = 3.79\ \mu\Omega\ \text{cm}, \tag{3}$$

a_0 being the first Bohr radius. Using (2), Eq. (1) can be integrated to give

$$\rho_s = (4\pi\hbar/100e^2k_F)\sum l|\gamma_{l-1}-\gamma_l|^2, \tag{4}$$

where

$$\gamma_l = (1/2i)(e^{2i\eta_l^1} - e^{2i\eta_l^0}). \tag{5}$$

The case of vacancies is particularly simple, for then all the η_l^1 are zero and (4) reduces to

$$\rho_v = (4\pi\hbar/100e^2k_F)\sum_1^\infty l \sin^2(\eta_{l-1}^0 - \eta_l^0). \tag{6}$$

This expression is conventionally applied[8] to *impurity* resistivities in which the Bloch waves of the unperturbed lattice are approximated by plane waves and the phase shifts calculated for the perturbing potential. From the present point of view, however, (6) applies to vacancies only, impurities being dealt with using (4). In this way some attempt is made to include band structure[9] in the sense that one considers scattering differences for absolute potentials rather than absolute scattering from potential differences.

Actually, in the present circumstances of monovalent impurities in monovalent matrices, small-angle expansions are appropriate and the basic formulas of the two approaches are analytically equivalent [cf. (6) and (9), below]. As we have indicated, however, the basic philosophy and thus the method by which the phase shifts are computed are very different.

The reason why small angle approximations are possible is that the Friedel rule[10] requires

$$(2/\pi)\sum(2l+1)\eta_l^j = 1 \tag{7}$$

and, since a screened ion is essentially attractive to electrons, the η's are positive or, at most, one or more may be very slightly negative. But no one phase shift can become too large, as this signals an electronic transition which invalidates the model. (This matter will be taken up in more detail in Secs. 4 and 5.) The effect, in general, is to obtain two or three small positive η's characterizing the pseudo-atom.

In our detailed calculations, we use the full expressions [such as (4) for solids], but approximate forms are very useful for qualitative interpretations of our final results. With this remark in mind, we proceed to the small-angle expansion of (4).

To first order, (5) becomes

$$\gamma_l \approx \eta_l^1 - \eta_l^0 \tag{8}$$

and, thus, (4) gives

$$\rho_s \approx (4\pi\hbar/100e^2k_F)\sum l(\gamma_{l-1}-\gamma_l)^2, \tag{9}$$

and this, to the approximation indicated, is of the same functional form as (6).

Now, as emerges in Sec. 5, it never happens that more than three pseudo-atom phase shifts are significant. Thus, observing from (7) and (8) that

$$\sum(2l+1)\gamma_l \approx 0, \tag{10}$$

we may substitute for γ_2, in terms of γ_0 and γ_1, in (9) and obtain

$$\rho_s \approx (4\pi\hbar/100e^2k_F)(36/5)(\gamma_1^2 + \tfrac{1}{6}\gamma_0^2). \tag{11}$$

In general, the first term shown is substantially larger than the second, and ρ_s is very roughly proportional to the square of the relative p-wave phase shift.

Conventionally, the relative phase shifts are evaluated for a particular solvent and a particular solute in the manner indicated above, but the Ziman approach enables one to tabulate, once and for all, η's from which the γ_l corresponding to any alloy may be readily deduced. It is appropriate to mention at this point that we have tackled a set of difficult cases, in that [cf. (10)] there is no valency difference between solvent and solute. When such does exist, invoking the sum rule has usually been found to be sufficient to ensure reasonable results for a rather wide variety of potentials.[8] (Only in the cases of vacancies, below, do we have valence differences; where comparison is possible, our results are in agreement with experiment, in conformity with the above remarks.)

Finally, it should be pointed out that lattice distortion has been ignored, Ziman having estimated this to incur errors of the order of 10%.

3. LIQUIDS

A. Dilatation Effects

In order to take into account the dilatation δ resulting from the insertion of a foreign atom into an otherwise pure metallic matrix, FZ have introduced a modified solute scattering amplitude

$$f_1'(\xi) = f_1(\xi) - \delta f(k_F\xi) f_0(\xi), \tag{12}$$

where

$$f(K) = \int_0^\infty (dP/dr)(\sin Kr/Kr)dr, \tag{13}$$

P being the radial distribution function, related to the pure liquid structure factor, α, through the equation

$$P(r) = 1 + (2\pi)^{-3}(V/N)\int_0^\infty [\alpha(q)-1] \times(\sin qr/qr)4\pi q^2 dq. \tag{14}$$

As usual, N and V denote the total number of ions and the total volume, respectively.

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[8] J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, England, 1960).

[9] Reference 1, p. 130.

[10] J. Friedel, Phil. Mag. 43, 153 (1952).

For given α, the problem arises of finding f. For the present work, P itself is of no direct interest, and its elimination from the theory brings about a reduction in the amount of numerical work involved. Thus, use of (14) in (13) gives:

$$f(k_F\xi)=\frac{3}{2}\int_0^\infty [\alpha(k_F\zeta)-1]I(\xi/\zeta)\zeta^2d\zeta\,, \qquad (15)$$

where[11]

$$I(y)=\int_0^\infty \frac{\sin yx}{yx}\frac{d}{dx}\left(\frac{\sin x}{x}\right)dx$$
$$=-\frac{1}{2}+\frac{1}{4}\left(y-\frac{1}{y}\right)\ln\left|\frac{y+1}{y-1}\right|\,. \qquad (16)$$

We have evaluated (15) for two structure factors: (i) the theoretical universal Ashcroft-Lekner[12] (hereafter AL) form and (ii) the experimental result[13] for liquid Na at its melting point. It is evident from Fig. 1 that the somewhat different long-range characters have little influence on f for $0\leq\xi\leq2$ (where $\xi=K/k_F$). As the AL α is known[12,14] to describe the region below the first peak adequately for resistivity calculations, and its deviations from physical behavior at large ξ have, evidently, no repercussions in f over the range (0,2) of interest in resistivity work, we conclude that we can proceed with confidence with the choice (i) indicated above.

The AL structure factor corresponds to an exact solution of the Percus-Yevick equation for hard spheres, with a packing fraction of 45%. In this way, the experimental first peaks for the alkalis and a number of other metals are fitted rather well. It will be seen, then, that there is a formal difficulty in defining dP/dr in (13): This can be handled conceptually by supposing, first, that we have a continuous interionic potential, integrating by parts, and then proceeding to the limit. In practice, no computational difficulties associated with this matter arise in (15), in contrast with what would have happened if we had evaluated P through (14).

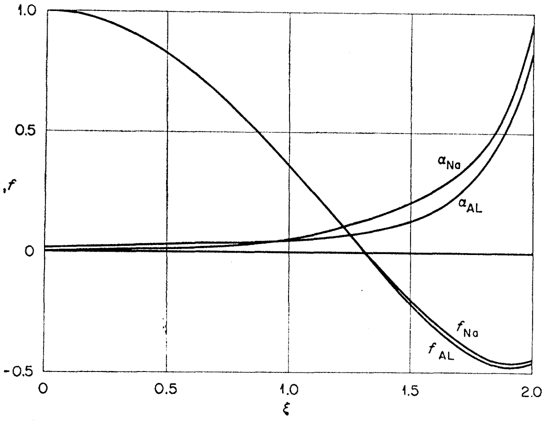

FIG. 1. Structure factors α and corresponding dilatation functions f versus $\xi(=K/k_F)$. Those subscripted Na correspond to the Gingrich-Heaton (Ref. 13) experimental data; the others arise from the hard-sphere model of Ashcroft and Lekner (Ref. 12).

B. Electron-Scattering Effects

Implicit in the FZ theory is a formula for the resistivity increment per atomic percent of impurity 1 added to a pure liquid metal 0. When generalized to the complex scattering amplitudes required here, it reads

$$\rho_l=\rho_1+\rho_2\,, \qquad (17)$$

where

$$\rho_1=(\lambda/a_0k_F)\int_0^2 |f_1'-f_0|^2\xi^3d\xi\,, \qquad (18)$$

and

$$\rho_2=(\lambda/a_0k_F)\int_0^2 (f_0^*f_1'+f_0f_1'^*-2|f_0|^2)\times\alpha(k_F\xi)\xi^3d\xi\,. \qquad (19)$$

In view of (1), (12), and (18), we see that $\rho_1=\rho_s$ when $\delta=0$.

Insertion of (12) into (18) gives

$$\rho_1=\rho_s+\rho_t\delta+\rho_u\delta^2\,, \qquad (20)$$

where

$$\rho_t=-(\lambda/a_0k_F)\int_0^2 f(f_0^*f_1+f_0f_1^*-2|f_0|^2)\xi^3d\xi\,, \qquad (21)$$

and

$$\rho_u=(\lambda/a_0k_F)\int_0^2 f^2|f_0|^2\xi^3d\xi\,. \qquad (22)$$

Similarly, use of (12) in (19) gives

$$\rho_2=\rho_m+\rho_n\delta\,, \qquad (23)$$

where

$$\rho_m=(\lambda/a_0k_F)\int_0^2 (f_0^*f_1+f_0f_1^*-2|f_0|^2)\alpha\xi^3d\xi\,, \qquad (24)$$

and

$$\rho_n=-2(\lambda/a_0k_F)\int_0^2 f|f_0|^2\alpha\xi^3d\xi\,. \qquad (25)$$

It will be noted that ρ_u and ρ_n are independent of solute and that (17) represents a downward-pointing parabola in δ with minimum described by

$$\delta_{\min}=-(\rho_t+\rho_n)/2\rho_u\,;\quad \rho_{\min}=\rho_l(\delta=0)-\rho_u\delta^2_{\min}\,. \qquad (26)$$

Once more, as in Sec. 2, we proceed at this stage to an approximate analysis of some of the above expressions in order to facilitate our interpretation of the computed results to be given later. A greatly simplifying feature is the form of f (see Fig. 1), which is not grossly varying in the larger-angle scattering region. Hence, it can be assigned its $\xi=2$ value and the resulting integrals may be further simplified and, in some cases, interpreted

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[11] We are grateful to F. Hawkins and Dr. L. Mirsky of the Sheffield University Mathematics Department for evaluating this integral.

[12] N. W. Ashcroft and J. Lekner, Phys. Rev. **145**, 83 (1966).

[13] N. S. Gingrich and L. Heaton, J. Chem. Phys. **34**, 873 (1961).

[14] W. H. Young, A. Meyer, and G. E. Kilby, I in this series.

physically. Thus, (22) becomes

$$\rho_u \approx f^2(2)\rho_v\,, \tag{27}$$

[cf. Eq. (1) and the comments preceding (6)], and this is a natural type of coefficient to expect in the large dilatation limit. Equation (25) is similarly interpreted as

$$\rho_n \approx -2f(2)\rho_{pl}/100\,, \tag{28}$$

where ρ_{pl} is the resistivity of the pure liquid.[1,12,14]

It turns out that the impurity resistivity change on melting depends little on dilatation, and thus ρ_m, its value at $\delta=0$, is of particular interest; it may be approximately written

$$\begin{aligned}\rho_m &\approx (\lambda/a_0k_F)\left(\int_0^2 \alpha\xi^3 d\xi\right)[f_0{}^*f_1+f_0f_1{}^*-2|f_0|^2]_{\xi=2}\\ &\approx (1152/9\pi^2)(\lambda/a_0k_F)\left(\int_0^2 \alpha\xi^3 d\xi\right)\gamma_1(\eta_1{}^0-\pi/12)\,,\end{aligned} \tag{29}$$

the final step involving small angle expansions and use of (7), (8) and (10). Thus, ρ_m is small if either γ_1 is small or $\eta_1{}^0 \approx 0.26$.

4. RESULTS

The relevant phase-shift data, taken from Meyer *et at.*,[4] are given in Table I. Thus, Eq. (4) may be used immediately to calculate impurity resistivities in the solids, and these are shown in Table III.

The calculation of the corresponding quantities in the liquids is more devious, however, because the precise value of δ to be taken in any given application is not known. Our aim, now, is to show that ρ_l is insensitive to the choice of δ and that quite crude values will suffice.

In Table II are shown some results calculated using Table I, the AL structure factor and the formulas of the previous section. They combine to show that for dilatations of interest (i.e., for $|\delta|$ up to about 2) the possible variations of ρ_l are never gross and, in most cases, are quite small. There appears to be no one simple explanation for this, but certain factors combine to make it possible.

First, as the final column of Table III indicates, $\rho_v \approx 1.25$ (all values being in $\mu\Omega$ cm/at.%), and, therefore, by (27) $\rho_u \approx 0.3$. Thus the coefficient of δ^2 in $\rho_l(\delta)$ is determined and this is usually small compared with ρ_s. Secondly, ρ_{pl} varies between about 10 and 50 for monovalent liquid metals, and so (28) gives ρ_n to be, at its largest, about 0.5 but usually very much less than this. Apart from ρ_n, the other contribution to the linear term in $\rho_l(\delta)$ is ρ_t. This is an interference term [cf. (21)] which is small if either $f_1 \approx f_0$ (for example, as in noble-metal–noble-metal systems) or if f_0 is small (as in Na, K, and Rb) in the backscattering region. In those cases (Li and Cs) when ρ_n is largest, the size of f_0 for large-angle scattering is responsible and thus, as is clear from (21) and (25), in such cases ρ_t will cancel against ρ_n. The upshot is that almost without exception the coefficients of δ and δ^2 are small compared with the constant term in $\rho_l(\delta)$, thus yielding a slowly varying function, insensitive to physical choices of δ.

TABLE I. Pseudo-atom phase shifts.

Metal	$k_F{}^a$	η_0	η_1	η_2	η_3
Li	0.332	0.870	0.228	0.004	0.000
	0.357	0.778	0.257	0.005	0.000
	0.382	0.697	0.282	0.005	0.000
	0.474	0.450	0.357	0.010	0.000
	0.578	0.243	0.417	0.015	0.001
	0.611	0.189	0.432	0.016	0.001
	0.614	0.185	0.433	0.016	0.001
	0.699	0.069	0.464	0.021	0.001
Na	0.332	0.966	0.188	0.008	0.000
	0.357	0.882	0.212	0.010	0.000
	0.382	0.809	0.232	0.013	0.000
	0.474	0.582	0.284	0.026	0.001
	0.578	0.388	0.311	0.047	0.002
	0.611	0.336	0.313	0.055	0.003
	0.614	0.332	0.313	0.055	0.003
	0.699	0.219	0.309	0.078	0.005
K	0.332	0.705	0.212	0.045	0.001
	0.357	0.618	0.215	0.060	0.001
	0.382	0.535	0.212	0.078	0.001
	0.474	0.254	0.143	0.174	0.002
	0.578	−0.014	0.010	0.307	0.003
Rb	0.332	0.662	0.195	0.063	0.001
	0.357	0.573	0.190	0.083	0.002
	0.382	0.490	0.178	0.106	0.002
	0.474	0.220	0.086	0.213	0.004
	0.578	−0.007	−0.051	0.338	0.006
Cs	0.332	0.445	0.122	0.149	0.002
	0.357	0.338	0.090	0.189	0.003
	0.382	0.239	0.051	0.231	0.003
	0.474	−0.047	−0.091	0.369	0.006
	0.578	−0.163	−0.186	0.441	0.012
Cu	0.474	0.983	0.197	−0.001	0.000
	0.578	0.785	0.264	−0.002	0.000
	0.611	0.730	0.282	−0.002	0.001
	0.614	0.726	0.284	−0.002	0.001
	0.699	0.603	0.324	−0.003	0.001
Ag	0.474	0.905	0.228	−0.005	0.000
	0.578	0.710	0.299	−0.009	0.001
	0.611	0.657	0.318	−0.011	0.002
	0.614	0.653	0.320	−0.011	0.002
	0.699	0.533	0.361	−0.015	0.004
Au	0.474	0.917	0.232	−0.009	0.001
	0.578	0.719	0.309	−0.018	0.002
	0.611	0.665	0.330	−0.021	0.003
	0.614	0.660	0.332	−0.021	0.003
	0.699	0.536	0.378	−0.028	0.006

[a] The k_F's are in atomic units. Those appropriate to the pure liquid metals at their melting points are given in Table IV.

Table II establishes lower bounds (by the present theory and data) to the various impurity resistivities. If the physical choice of δ is positive, one chooses $\rho_{\min}$ if $\delta_{\min}>0$ and $\rho_l(\delta=0)$ if $\delta_{\min}<0$. A similar selection is made if δ is negative and the lower bounds thus found are italicized in the table.

To improve on the above a little, we have taken

$$\delta \approx (k_F{}^0/k_F{}^1)^3 - 1\,, \tag{30}$$

where the k_F's are the respective pure liquid values, as given in Table IV. This supposes that the volume associated with an ion is unaltered by its environment; it is

TABLE II. Dilatation data.[a]

Solvent	Solute	ρ_s	ρ_t	ρ_m	$\rho_l(\delta=0)$	$\rho_{\min}$	$\delta_{\min}$
Li	Na	0.47	−0.61	−0.75	−0.28	*−0.28*	0.12
(0.363)	K	5.69	−1.39	−2.45	3.25	*2.72*	1.20
[0.516]	Rb	7.20	−1.62	−2.79	4.41	*3.57*	1.52
	Cs	11.48	−1.92	−3.43	8.06	*6.70*	1.93
	Cu	2.25	−1.13	−1.21	*1.04*	0.78	0.85
	Ag	1.62	−0.95	−0.98	*0.64*	0.51	0.60
	Au	1.58	−0.91	−0.91	*0.67*	0.57	0.55
Na	Li	0.33	−0.06	−0.01	*0.32*	0.32	0.05
(0.225)	K	1.55	−0.01	−0.39	*1.16*	1.16	−0.06
[0.032]	Rb	2.48	0.00	−0.49	*1.99*	1.99	−0.08
	Cs	8.00	0.04	−0.83	*7.17*	7.17	−0.17
	Cu	1.16	0.24	0.20	1.36	*1.27*	−0.61
	Ag	0.74	0.18	0.18	0.92	*0.87*	−0.47
	Au	0.77	0.19	0.20	0.97	*0.92*	−0.49
K	Li	0.50	−0.13	−0.04	*0.46*	0.45	0.15
(0.239)	Na	0.67	0.07	0.14	0.82	*0.80*	−0.27
[0.062]	Rb	0.07	0.08	0.04	*0.11*	0.09	−0.30
	Cs	2.08	0.36	0.12	*2.19*	2.01	−0.89
Rb	Li	0.67	−0.13	−0.06	0.61	*0.61*	−0.04
(0.291)	Na	0.92	0.11	0.17	1.08	*1.02*	−0.46
[0.155]	K	0.05	−0.07	−0.05	0.01	*0.00*	−0.14
	Cs	1.11	0.26	0.12	*1.22*	1.08	−0.71
Cs	Li	2.62	−0.64	−0.76	*1.86*	1.84	0.19
(0.359)	Na	3.02	−0.38	−0.51	2.51	*2.50*	−0.16
[0.499]	K	1.24	−0.54	−0.61	*0.62*	0.62	0.06
	Rb	0.84	−0.43	−0.49	0.35	*0.35*	−0.09
Cu	Li	1.76	0.11	0.08	1.84	*1.79*	−0.48
(0.187)	Na	0.64	0.01	−0.17	0.48	*0.47*	−0.22
[0.074]	Ag	0.06	0.02	0.05	*0.11*	0.10	−0.25
	Au	0.11	0.04	0.09	*0.20*	0.18	−0.30
Ag	Li	1.52	−0.04	−0.07	1.44	*1.44*	−0.14
(0.229)	Na	0.53	−0.07	−0.23	0.31	*0.31*	−0.06
[0.102]	Cu	0.06	0.01	−0.02	0.04	*0.03*	−0.25
	Au	0.01	0.01	0.04	0.04	0.03	−0.25
Au	Li	1.46	0.00	−0.05	1.41	*1.39*	−0.28
(0.245)	Na	0.57	−0.08	−0.27	0.30	*0.30*	−0.11
[0.133]	Cu	0.09	−0.17	−0.08	0.01	*0.00*	−0.24
	Ag	0.01	−0.02	−0.04	−0.04	−0.05	−0.24

[a] All numbers are in $\mu\Omega$ cm/atomic percent. The above figures demonstrate the insensitivity of ρ_l [cf. (17) and thereafter] to variations of δ. The italicized numbers represent lower bounds to ρ_l consistent with the FZ theory and the data of Table I (see early paragraphs of Sec. 4) and are not greatly different from the ρ_l's of Table III calculated using an improved (though possibly still crude) choice of δ. The entries under the solvents are ρ_u [cf. (22)] and ρ_n [cf. (25)] in round and square parentheses, respectively.

an empirical assumption, but in reasonable accord with Freedman-Robertson[15] data for Na alloys, and, as we have stressed, its effects are not radical. The ρ_l thus computed are shown in Table III.

A discussion of the theoretical and experimental numbers shown in Table III occupies the remainder of this section, and, for this purpose, it will be convenient to partition the data in the manner indicated in the following subsections.

A. Alkalis in Alkalis

Here, the over-all comparison with experiment is quite good. The poorer values involve Cs, and this is consistent with the observation[4] that η_2 data for this case, as a result of a certain computational approximation, tend to be overestimated. Bearing in mind (8) and (10), a glance at the relevant lines of Table I shows quite clearly that a reduction in η_2 for Cs will decrease γ_0 and γ_1 and, thus, ρ_s as given by (11). Furthermore, since it is principally determined by ρ_s, we can expect the same kind of errors to occur in ρ_l. As Table I indicates, the errors in η_2, for Cs, increase as the Fermi level is raised and this is in line with the sizes of the discrepancies between theory and experiment for the three systems, Cs in Na, Cs in K, and Rb in Cs, under discussion. In the other cases, where experimental values are not available, we can also expect results to be too large, particularly when higher Fermi levels are involved.

It will also be seen that in the three cases where experimental data are available, the *change* in impurity resistivity on melting is reasonably described. This increases for the cases of Na and Rb in K and decreases for K in Rb, and the reasons for these two possible kinds of behavior may be sought, as follows, in the variation of the phase shifts.

As has been shown, the effect of dilatation is small. Thus, let us consider $\rho_l(\delta=0)-\rho_s=\rho_m$, which is given exactly by (24) and approximately by (29). For Na in K, γ_1 is so small ($=0.020$, see Table I) that higher-order terms omitted from (29) are required to represent (24). However, (29) describes the other two cases satisfactorily. For Rb in K, Table I gives $\gamma_1=-0.034$ and $\eta_1{}^0-\pi/12=-0.047$, and thus ρ_m is positive. On the other hand, for K in Rb, we find $\gamma_1=0.025$ and $\eta_1{}^0-\pi/12=-0.072$, and so ρ_m is negative.

Actually, the case of K in Rb is an illustration of the possibility that in the liquid (as distinct from in the solid) the impurity resistivity can be negative. This occurrence is less rare when polyvalent metals are involved and happens, in present circumstances, as the result of a number of exacting conditions being met. First, as we saw above, the η_1's are such that ρ_m is negative. But this is not enough if ρ_s is too large. In fact, Rb and K scatter very much like solvent ions when inserted as impurities into each other, as is indicated by the appropriate ρ_s values in Table III. In order to obtain such small ρ_s's it is necessary [see (11)] that *both* γ_0 and γ_1 should be small. Thus, for example, as we have seen above, γ_1 is very small for Na in K, but the corresponding $\gamma_0=0.274$ is quite large compared with the K in Rb and Rb in K *s*-wave values of ±0.045.

Among the cases under study, that of Na in Li would appear to be the best (and, indeed, only other) example for exhibiting a negative ρ_l. Here, the root cause is somewhat different from that discussed above, lying in the relatively large *p*-wave phase shift for Li when acting as a solvent. This means that $\eta_1{}^0-\pi/12$ is positive and γ_1 is negative for each solute, both terms being unusually large in absolute value. Thus (29) predicts a strong negative ρ_m, which, when Na is the solute, is sufficient to make $\rho_s+\rho_m$ negative. Unfortunately, the experiment has not yet been performed.

Agreement with observation is satisfactory for the alkalis in liquid Na, particularly when the above discussion concerning Cs is recalled, though it is, perhaps,

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[15] J. F. Freedman and W. D. Robertson, J. Chem. Phys. 34, 873 (1961).

TABLE III. Theoretical and experimental impurity resistivities. All numbers are $\mu\Omega$ cm/at.%. The theoretical results marked with an asterisk mean that, on the basis of Table IV an s-wave resonance should occur, and the present work will severely underestimate the correct value. Table I indicates the possibility of p- and d-wave resonances, also, and these are indicated by ** and ***, respectively. In each unit the values are placed according to the following key:

Solid, theoretical; Eq. (1)	Liquid, theoretical; Eq. (17)
Solid, experimental	Liquid, experimental

Solvent \ Solute	Li		Na		K		Rb		Cs		Vacancy
Li			0.47	−0.11	5.69	3.30	7.20***	4.65***	11.48***	8.71***	1.59
Na	0.33	0.37			1.55	1.37	2.48	2.44	8.00	8.14	1.26
		0.28^{a}				1.02^{a}		2.55^{a}		3.64^{a}	
K	0.50	0.63	0.67	0.81			0.07	0.16	2.08	2.48	1.10
			0.56^{b}	1.1^{c}			$0.11^{d,b}$	0.21^{b}	1.1^{k}		
Rb	0.67	0.76	0.92*	1.02*	0.05	0.00			1.11	1.34	1.40
					0.04, 0.13^{e}	-0.03^{d}					
Cs	2.62	2.20	3.02*	2.56*	1.24	0.68	0.84	0.35			1.37^{d}
							0.28^{e}				

	Li		Na		Cu		Ag		Au		
Li					2.25	1.38	1.62	0.71	1.58	0.75	
					1.16*	1.27*	0.74*	0.87*	0.77*	0.92*	
								2.50^{a}		4.80^{a}	
Cu	1.76**	2.09**	0.64	1.57			0.06	0.20	0.11	0.29	1.10
							0.07^{j}	0.07^{f}	0.52^{g}	0.48^{f}	1.5^{h}
Ag	1.52	1.46	0.53	0.64	0.06	0.03			0.01	0.04	1.43
					0.08^{i}	0.08^{f}			$0.36^{g,i}$	0.45^{f}	1.3^{h}
Au	1.46	1.45	0.57	0.70	0.09	0.00	0.01	−0.04			1.53
					0.36^{j}	0.16^{f}	0.36^{j}	$0.3(3)^{f}$			1.5^{h}

[a] J. F. Freedman and W. D. Robertson, J. Chem. Phys. **34**, 769 (1961). At the melting points.

[b] A. M. Guénault and D. K. C. MacDonald, Proc. Roy. Soc. (London) **A264**, 41 (1964). Measurements were quoted for 4.2°K in terms of room-temperature values. We have taken the ideal resistivity of pure K at room temperature to be that obtained by J. S. Dugdale and D. Gugan [Proc. Roy. Soc (London) **A270**, 186 (1962)].

[c] C. C. Bradley, Phil. Mag **7**, 1337 (1962). At 500°K; the figure shown, therefore is likely to overestimate that appropriate to the melting point [cf. further results reported in Ref. a].

[d] N. S. Kurnakow and A. J. Nikitinsky, Z. anorg. Chem. **88**, 151 (1914). The figures are for 298°K for the solids and 348°K for the liquids.

[e] A. M. Guénault and D. K. C. MacDonald, Proc. Roy. Soc. (London) **A274**, 154 (1963). At 4.2°K. The ideal resistivities [cf. Ref. b] of pure Rb and Cs have been taken to be those given by J. S. Dugdale and D. Phillips [Proc. Roy. Soc. (London) **A287**, 381 (1965)].

[f] A. Roll and H. Motz, Z. Metalkde. **48**, 495 (1957). At the melting points.

[g] L. D. Roberts, R. L. Becker and F. E. Obenshain, Phys. Rev. **137**, A895 (1965). Professor J. S. Dugdale (private communication) has made measurements in essential agreement with these figures.

[h] As quoted by J. Friedel, in *The Interaction of Radiation with Solids*, edited by R. Strumane, J. Nihoul, R. Gevers, and S. Amelinckx (North-Holland Publishing Company, Amsterdam, 1964).

[i] J. O. Linde, Ann. Physik **15**, 219 (1932).

[j] J. S. Dugdale (private communication). Professor Dugdale has indicated that these results are rather less reliable than those of Ref. g.

[k] M. A. Archibald, J. E. Dunick, and M. H. Jericho, Phys. Rev. **153**, 786 (1967).

worth remarking that in this series ρ_s, alone, dictates the trend.[16]

Finally, we should mention the possibility of resonances for the cases of Na in Rb and Cs and also of K, Rb, and Cs in Li, but, for convenience, we postpone the discussion of this matter until later.

B. Noble Metals in Noble Metals

As Table III shows, results are poor here, particularly when Au is used. The trouble would not appear to be one of numerical accuracy (successful calculations for some of the alkali-alkali systems being at least as delicate), and thus we conclude that the physical model is at fault for such systems.[2] We should point out, however, that pure liquid-metal resistivities and thermopowers,[14] vacancy resistivities [see 4C below] and divacancy binding energies[17] are given reasonably by the pseudo-atom approach.

C. Noble Metals in Alkalis

There occurs here another kind of situation which invalidates our quoted results under certain circumstances. This is when an electronic transition is involved.

By investigating the lowest free-electron wave function in the pseudo-atom model problem of Sec. 1, it is possible[18] to establish that Fermi wave index $k_F{}^c$ below which an additional bound s state is formed. The results found by Meyer *et al.*[4] are shown in Table IV and should give an indication of where similar bound states occur in alloys.

When such a bound state occurs, the corresponding phase shift changes by π, and the data of Table I are based on the assumption that this happens discontinu-

TABLE IV. Pseudo-atom bound states.

Metal	Li	Na	K	Rb	Cs	Cu	Ag	Au
$k_F{}^c$ [a]	0.27	0.35	0.28	0.29	0.24	0.50	0.49	0.53
k_F	0.578	0.474	0.382	0.357	0.332	0.699	0.611	0.614

[a] $k_F{}^c$, in atomic units, gives that Fermi level at which a pseudo-atom acquires an additional bound s state. k_F, also in atomic units, corresponds to the pure liquid at the melting point.

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[16] In Ref. 5 we quoted results appropriate to the experimental α of Ref. 13 and the f drawn in Fig. 2 of Ref. 3. This accounts largely for small differences from the present numbers.

[17] Axel Meyer, W. H. Young, and J. M. Dickey (to be published).

[18] A. Messiah, *Quantum Mechanics* (North-Holland Publishing Company, Amsterdam, 1961), Vol. I, pp. 392, 408.

ously at $k_F{}^c$. In practice, however, in some fairly narrow region of k_F above $k_F{}^c$, the system will possess a virtual bound state, and a rapid, but nevertheless continuous, variation of η_0 with k_F will take place. This results in considerably enhanced scattering not accounted for by the present techniques.

Table IV indicates that Ag may have a virtual bound state in Na and provides an explanation of why our calculated ρ_l so severely underestimates the observed value. Presumably, a similar explanation may apply to Au in Na.

The calculated results for Li as solvent are displayed in Table III because, if the above reasoning is the whole story, we can expect these predictions to be correct. On the other hand, the K, Rb and Cs solvent cases are omitted because, as indicated above, the underlying model is no longer obviously correct.

In view of Table IV and the above discussion, the significance of the final paragraph of Sec. 4A, insofar as it affects Na in Rb and Cs, is now apparent.

D. Alkalis in Noble Metals

In these cases, electronic transitions of a different character appear to be possible. It will be seen from Table I that at higher k_F the screening charge for K, Rb and Cs is almost all of d character. We might thus expect a situation somewhat analogous to that discussed in Sec. 4C for s waves, and, indeed, there appears to be indirect evidence in favor of this conclusion in Fermi's explanation[19] of the sharp increase in the resistivity of pure Cs obtainable under pressure.

We have not investigated the situation in a manner comparable to that of Sec. 4C, and have no analog of Table IV. We assume, however, on the basis of the Table I data, that the computational techniques of Meyer *et al.*[4] are not applicable to K, Rb and Cs at Fermi levels as high as those in the noble metals. Li is more marginal and theoretical numbers are quoted, but η_1 is uncomfortably high. From the present point of view, the application to Na would appear to be more reasonable.

A similar situation may occur [recall end of Sec. 4B] for K, Rb and Cs in Li, but in the case of Cs (and, to a lesser extent, Rb when, as in present circumstances, the Fermi level is quite high) the known[4] overestimation of η_2 results in our present calculations already being too high.

E. Vacancies

Here, one may use Table I and Eq. (6) to obtain the final column of Table III, the agreement with experiment being satisfactory where comparison is possible. This is a difficult problem from the perturbative approach,[20] the perturbation resulting from the creation of a vacancy being large. By the present method, there is no special trouble and reasonable results are actually easier to obtain for vacancies than for monovalent impurities. For, as Table III illustrates, a variety of sets of phase shifts all satisfying (7) give about the same ρ_v, whereas the γ's satisfying (10) are seen to give rise to a wide range of ρ_s's. In short, a valency difference helps enormously.

5. DISCUSSION

Our results for alkali-alkali systems are encouraging. Insofar as comparison with experiment is possible, they are consistent with the conclusion that the pseudo-atom picture of Ziman[1] and Harrison[2] and the liquid-metal alloy theory of FZ are valid.[3] To get the details correct (as we have done) for the systems Na in K, Rb in K, and K in Rb both for the solids and the liquids, requires a high level of numerical accuracy in the phase shifts, as was shown in Sec. 4(a). This suggests that the phase shifts of Meyer *et al.*[4] are rather accurate for Na, K, and Rb. For Cs they are less so, though fairly small reductions in the $\eta_2(k_F)$ for this ion would bring the corresponding computations into line with experiment.

As we indicated in Sec. 4E, cases when there is no valency difference between solvent and solute are difficult to treat and extreme numerical accuracy is demanded. The fair success of the alkali η's for present purposes suggests that they may be applied, with confidence, to less critical situations.

In contrast with the above, the present approach appears to be inappropriate, on physical grounds, to noble-metal–noble-metal systems. We leave the degree of applicability of the present techniques to alkali-noble-metal systems open. The difficulty (and the interest) here lies in the possibility of the formation of bound and virtual bound states, invalidating the model on which the present phase shifts are calculated.

Finally, it is important to indicate the extent to which the FZ theory has been tested in the present work. This theory is rather general, extending over all composition ratios for binary alloys, whereas we are concerned only with the small concentration limits. In addition, whereas FZ invoke three structure factors, we use only that for the pure solvent into which the impurity is inserted.

Also, our results are insensitive to dilatation (and, thus, despite obvious size differences among the various ions, the FZ "substitutional" model is valid in the low-impurity concentration limit). The advantage of this is that despite our poor knowledge of dilatation, meaningful impurity resistivities can be obtained; the disadvantage is that the particular mechanism employed by FZ for including this effect has not been tested.

On the other hand, their disorder term, under conditions of zero dilatation, has been successfully applied and explains clearly why the impurity resistivity changes on melting for the three cases (under present discussion) where experimental results are known.

ACKNOWLEDGMENT

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[19] I. G. Austin, Contemporary Physics 7, 174 (1966). See p. 185.

[20] J. Friedel, in *The Interaction of Radiation with Solids*, edited by R. Strumane, J. Nihoul, R. Gevers, and S. Amelinckx (North-Holland, Amsterdam, 1964).