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Spin-Flip Scattering Cross Section for Conduction Electrons of Foreign Atoms in Lithium and Sodium. II*

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We calculate spin-flip scattering cross sections for conduction electrons of a number of impurities in metallic lithium and sodium, in order to improve on the results reported in our earlier paper. The method uses the numerical integration of a potential which is derived from the Herman-Skillman atomic potential near the impurity, and is flat beyond a suitably chosen radius. Screening is included by requiring that the Friedel sum rule be satisfied. No parameters of the theory are adjusted to fit experimental data. The agreement for resistivity, Knight shift, and spin-flip scattering cross section is good for valence differences between impurity and host of 1 or 2. The theory gives a maximum in the cross section as the valence increases, but places the maximum at a valence difference of 4 instead of the experimentally observed value of more nearly 2.

I. INTRODUCTION

In the previous paper,[1] hereafter known as I, we described the results of experiments on the relaxation time of ESR in the metals lithium and sodium, which contained known amounts of impurities. The relaxation rates varied linearly with the concentration of impurities, so that the results could be given (see Table I) in the form of a spin-flip scattering cross section per impurity. The relaxation processes due to the pure metal are very small,[2,3] so that any effects of the impurity on these relaxation processes can be neglected. Thus, the relaxation comes mainly from the interaction of the conduction-electron spin with its orbital motion in the electric field of the impurity (spin-orbit coupling). In I it was shown that only the conduction electrons in the vicinity of the Fermi surface contribute to the relaxation, and therefore, since the spin-orbit interaction occurs well inside the ion core of the impurity, these measurements provide information about how the conduction electrons at the Fermi energy behave in the vicinity of the impurity nucleus.

To explain the results in I, we formulated a simple theory in which the spin-orbit coupling was considered as a perturbation on the orbital and spin motion of the electron. Outside the range of the impurity, the conduction electrons were considered as free.[4] If there is no valence difference between the solute and the solvent, one might hope that in the first approximation the effect of the impurity on the motion of the electron is negligible. We therefore assumed that the wave function of the electron is a plane wave orthogonalized to the core states of the impurity. If, however, there is a valence difference, the conduction electrons are strongly affected and move to screen out the different charge of the impurity core, so that, at large distances from the impurity, a conduction electron will not feel the charge difference. In I we tried to take this effect into account by assuming a Fermi-Thomas potential[5] for the impurity and numerically integrating to get the smooth part of the orbital state of the electrons. By orthogonalizing this smooth part to the core states of the impurity, an approximation to the actual state of the electrons was obtained.

The spin-flip cross section is related to the spin-orbit coupling matrix element which is calculable once the state of the electron and the experimentally measured core spin-orbit splittings of the impurities are known. As the valence difference is increased from −1 to +2, both the experimental (in all cases except thallium in lithium) and the theoretical results increased together;

Table I. Perturbation phase shifts, and cross sections and experimental cross sections.

	Phase shifts			Cross sections (10^{-17} cm^2)		
	δ_0	δ_1	δ_2	p	d	Expt
*Li*Mg	0.569	0.305	0.018	2.5×10^{-3}	...	6.4×10^{-4}
*Li*Al	1.094	0.65	0.019	1.48×10^{-2}	...	1.6×10^{-3}
*Li*Zn	0.813	0.259	−0.004	0.102	...	0.068
*Li*Cu	1.249	0.623	0.006	0.63	...	0.15
*Li*Pd	−0.126	−0.01	−0.283	0.12	26.8	0.2
*Li*Ag	0.054	0.049	−0.04	0.298	0.005	0.35
*Li*Cd	0.688	0.317	−0.011	1.47	...	0.75
*Li*In	1.052	0.69	0.004	5.85	...	1.0
*Li*Sn	1.313	1.11	0.014	14.6	...	0.22
*Li*Pt	−0.411	−0.082	−0.183	1.18	6.58	2.5
*Li*Au	0.098	0.059	−0.054	3.55	0.4	6.8
*Li*Hg	0.681	0.333	−0.021	16.15	0.03	11
*Li*Tl	1.106	0.673	0.005	67.78	...	8.9
*Li*Pb	1.208	1.152	0.01	102.6	...	1.6
*Na*Cd	0.902	0.238	−0.007	0.56	...	0.66
*Na*In	1.282	0.623	−0.002	3.8	...	2.3
*Na*Sn	1.428	1.086	0.005	12.05	...	0.28
*Na*Au	0.143	0.035	−0.047	1.07	0.36	2.9
*Na*Hg	0.86	0.271	−0.019	10.8	0.03	9.6
*Na*Tl	1.238	0.648	−0.005	33.8	...	27
*Na*Pb	1.417	1.091	0.004	87	...	20

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[1] J. R. Asik, M. A. Ball, C. P. Slichter, preceding paper, Phys. Rev. **181**, 646 (1969).

[2] R. J. Elliot, Phys. Rev. **96**, 266 (1954).

[3] Y. Yafet, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., London, 1963), Vol. 14.

[4] C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1964).

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

but when the valence difference became +3, the experimental results decreased while the theoretical ones increased. It was to justify the method used in I and to try to explain this discrepancy that the present calculations were undertaken.

Two sets of calculations are presented here. The first set, as in I, treats the spin-orbit coupling as a perturbation, whereas the second set treats it directly and exactly. This was done to test the possibility[6] that the conduction-electron spin has precessed through more than half a revolution while in the vicinity of the impurity. It can be argued from the experimental results, and also shown by the theoretical results, that this does not happen.

The aim of the paper is to present a better physical model of an impurity in a metal by trying to find, in the region around the impurity, the actual potential experienced by an electron with the Fermi energy. No local potential can do this exactly, but the potentials used here should improve on the Fermi-Thomas and square-well approximations. In particular, the potentials should include much of the true "chemical" nature of the impurity, the sort of effects that give rise to the positions in energy of the states of various electron angular momentum, so important in determining valence. The Fermi-Thomas potential, for instance, is well known to be a bad approximation when large valence differences are involved, and approximates the impurity by a point charge, thus neglecting the core of the impurity. This may be important in the screening effect, since the screening must take place mainly outside this core region, because the conduction electrons do not penetrate the core.

Far from the impurity, the conduction electrons are treated as free,[7] i.e., their wave functions can be taken to be plane waves. The band structure of the metal is supposed to be perturbed rigidly,[7,8] is otherwise unaffected by the impurities, and is assumed to be spherical. The results of Ham[9] are used (see Table II). The potential due to the impurity is assumed to be spherically symmetric, and thus the Hamiltonian for a conduction electron has full spherical symmetry. The state of such an electron can thus be classified by its energy and by its total angular momentum (J^2 and J_z) about the impurity. The total-angular-momentum quantum number j can be written in terms of the orbital angular momentum l,

$$j=l\pm\tfrac{1}{2}. \tag{1}$$

In the region outside the impurity, the wave function, classified by E_F, j, and l, is

$$(2j+1)[\cos\delta_j{}^l\, j_l(k_Fr)-\sin\delta_j{}^l\, n_l(k_Fr)], \tag{2}$$

where $j_l(r)$ and $n_l(r)$ are spherical Bessel functions.[10] The wave function (2) is properly normalized. $\delta_j{}^l$ is the phase shift for the total angular momentum j and orbital angular momentum l, and is found by making the wave functions and their first derivatives continuous at the boundary of the two regions. It is usual for all but the s-, p-, and d-wave phase shifts to be so small that they can be neglected. We calculated the f-wave phase shift in three cases and found it to be negligible in all three.

TABLE II. Parameters used in the calculations.

	Lithium	Sodium
Bottom of band[a]	−0.683 Ry	−0.604 Ry
Fermi energy[a]	−0.422 Ry	−0.367 Ry
k_F	0.5754	0.4868
m^*	1.32	1

[a] Relative to the zero of the atomic potential.

By integrating numerically outwards from the origin at the Fermi energy E_F, the shape of the wave function for a particular value of j and l can be determined. Its amplitude and the phase shifts are found by joining the wave function to (2). Thus, the matrix elements and the spin-flip scattering cross sections can be computed.

It is of interest to see how the phase shifts vary as the valence difference between the solute and the solvent varies, so that we have calculated phase shifts in the gold row of the periodic table up to valence differences of 6. The phase shift is essentially a measure of how much extra electronic charge of that momentum is present in the vicinity of the impurity. Odle and Flynn[11] have argued that the unit cell around the impurity resembles that around the free atom, and that an impurity is unlikely to attract more than a total of two s-like electronic charges around it before there is a significant amount of p-like and possibly d-like electronic charge. They have used this argument to explain their own Knight-shift measurements. These ideas disagree with the results of Kohn and Vosko[12] in their explanation of the experimental results of Rowland[13] on nuclear resonance intensity of copper with impurities. They only considered s- and p-wave phase shifts and calculated them using the Friedel sum rule and experimental values of the resistivity. They found that the s-wave phase shift increased rapidly with valence difference to values about π for valence differences of 3 and 4. This would suggest that there was a total s-like electronic charge of 3 around the impurity. We hope that our calculations will shed some light on the controversy, and this is discussed in Sec. VII.

Ferrell and Prange[14] have recently attempted to explain the experimental results by postulating that it is

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[9] F. Ham, Phys. Rev. **128**, 2524 (1962).

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[11] F. L. Odle and C. P. Flynn, Phil. Mag. **13**, 699 (1966).

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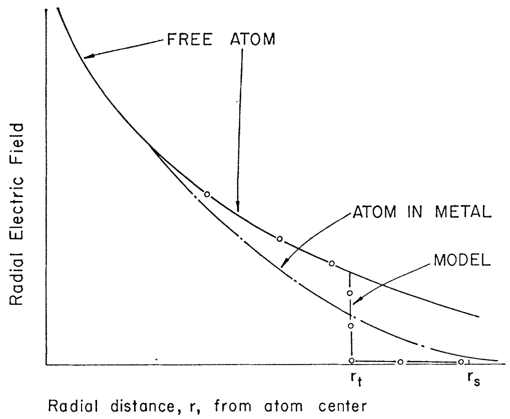

FIG. 1. Radial electric field versus radius for an impurity atom (a) as a free atom, (b) when imbedded in a metal, and (c) as approximated in the model of this paper.

only the p electrons that are involved in the screening, and that a drop in the spin-flip cross section will occur when the p resonance passes through the Fermi energy. This latter is bound to occur, but if the Odle-Flynn model is correct, it is not likely to occur until the valence difference is 4, if the solvent is monovalent. This result is confirmed in our calculations. Vassel's experiments[15] on the resistance due to impurities in copper also confirm the conjecture: When the impurities require s- and p-like electronic screening, the maximum resistance occurs at a valence difference of 4. We shall discuss this further in Sec. VII.

As reported earlier,[6] these calculations have been unable to explain the position of the drop in the experimental results as a function of valence. The agreement at small valence differences (with no adjustable parameters) suggests that the potentials used are not too inaccurate; it would seem that the discrepancy arises from the assumptions of the model, which may be untenable for large valence differences. We shall discuss this further in Sec. VII.

The plan of the paper is as follows: In Sec. II we consider the potential due to the impurity and in Sec. III the method of computation. Both of these are essentially the same in the two sets of calculations. In Secs. IV and V the theory and results for the perturbation procedure and the strong-coupling procedure, respectively, are presented. In Sec. VI these phase shifts are used to compute resistivities for various alloys where experimental results are available; these provide a further test for the phase shifts and potentials. Section VII summarizes the results, and Sec. VIII gives the conclusions.

II. POTENTIAL

If the exchange effect between electrons is neglected, the potential that an electron experiences can be derived from the electric field. Near the core of the atom, the electric field must be closely similar to that in the free atom. Far away from the atom the electric field vanishes as a result of screening. In the metal the screening will cause the electric field to drop to zero more rapidly than the $1/r^2$ of a Coulomb field. These facts are illustrated in Fig. 1. It may even be that the electric field is essentially zero at the radius r_s of the Wigner-Seitz sphere.

For sodium we have approximated the screening by an electric field shown in Fig. 1. (A slight modification was made for Li as described in Sec. III.) The properties are that the electric field is identical to the free atom out to a radius r_t and is zero beyond. We fix the value of r_t uniquely by numerically calculating the scattering phase shifts for electrons at the Fermi energy for various trial values of r_t and choosing that value for which the phase shifts satisfy the Friedel sum rule.

To carry out the phase-shift calculations we must first integrate the electric field to find the potential. For the model, the potential is identical to that of the atom inside r_t (apart from a constant A which shifts the zero of potential) and is flat beyond. It is continuous across the boundary but has a discontinuous slope. Beyond r_t the potential corresponds to the bottom of the conduction band. We calculate the phase shifts by numerical integration of the Schrödinger equation at an energy equal to the Fermi energy E_F above the bottom of the conduction band.

For an atom of valence Z, the Friedel sum rule states that to gain electrical neutrality the phase shifts of electrons with orbital angular momentum l and total angular momentum j must obey the equation

$$\frac{2}{\pi}\sum_{j,l}(2j+1)\delta_j{}^l=(Z-1), \tag{3}$$

which reduces, in the perturbation procedure, to the well-known Friedel sum rule. [In Appendix A, (3) is proved in the strong-coupling case.[7,8]] The constant A is then varied until the phase shifts satisfy (3).

Since the potential must be continuous, r_t must vary with the impurity. With sodium as a solvent, this can be easily accomplished because the effective mass of the conduction electrons is almost 1.[9] In lithium, however, the effective mass is 1.32,[9] which comes from the behavior of the electrons in the pure metal being different from free-electron behavior. To make the calculations consistent with the free-electron calculation of Ham,[16] the position of r_t should be fixed. These difficulties will be discussed in Sec. III.

The atomic potentials used were those of Herman and Skillman.[17] These are potentials that one electron would have if it were an electron of the free nonionized atom. Thus, we are assuming that the electronic correlation near the impurity in the metal is the same as that for the free atom. This is definitely not true, although

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[15] C. R. Vassel, J. Phys. Chem. Solids 7, 90 (1958).

[16] F. Ham, Solid State Phys. 1, 127 (1955).

[17] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).

the screening density for an ion in a pure metal is similar to that in the atom.[18] The Herman-Skillman potentials take some account of screening by using Slater's approximation[19] for exchange.

None of the approximations made is easily justifiable. They have the advantage of simplicity and of containing no parameters which are adjusted to fit the data. Nevertheless, we believe that we have taken account of the gross features due to screening by insisting on the satisfaction of the Friedel sum rule. We presume that the other factors are not important, and, as we shall see, the phase shifts and scattering cross sections are not very sensitive to the actual shape of the potential.

III. METHOD OF COMPUTATION

The shape of the wave function for an electron with a given angular momentum and at the Fermi energy is derived by numerically integrating Schrödinger's equation outwards from the origin. The first two values come from a series approximation and the rest by using the Noumerov method of numerical integration.[20] Accuracy was tested by halving the various intervals involved.

The magnitude of the wave function and the phase shifts are obtained by matching the wave function and its derivative to the free-electron wave function[2]; this was done at both r_t and r_s. It was found, however, that the two sets of phase shifts differed and that the Friedel sum could differ by as much as $\frac{1}{2}$ rad. Since the potential between r_t and r_s is flat, there should be no difference between the phase shifts at r_t and r_s.

The reason for the difference is that there is a discontinuity in the derivative of the potential at r_t. Thus, from Schrödinger's equation there should be a discontinuity in the third derivative of the wave function. The Noumerov method, since it used a Taylor expansion, assumes that the wave function is continuous in all derivatives up to the sixth. Using the Noumerov method around a discontinuity in the potential is equivalent to solving an equation different from the Schrödinger equation and is thus incorrect; the phase shifts at r_t must thus be used.

There is another problem associated with the effective mass of lithium. The nonunit effective mass means that the integration inside the impurity potential is done at an energy E above the bottom of the conduction band, but the integration outside the impurity potential is done at an energy E/m^*, where m^* is the effective mass. The location of the impurity boundary affects the measurement of the phase shifts quite considerably. Thus, we took the boundary as fixed at the same place ($r=2.9$ a.u.) as Ham took the boundary of the lithium atom. If the potential of an impurity was still deeper than the bottom of the lithium band, this is equivalent to imposing a finite discontinuity at 2.9 a.u. However, such discontinuities were small. If the potential of an impurity were such that $r_t<2.9$ a.u., the difficulties of the Noumerov method were ignored, and the phase shifts were again measured at $r=2.9$ a.u. This difficulty over the effective mass will always arise when we work with a free-electron theory. Such problems do not arise for sodium, since the sodium effective mass is unity. Then we can take r_t to be value of r when $V(r)=-0.604$ Ry.

IV. PERTURBATION METHOD

If the spin-orbit coupling is small, it can be considered as a perturbation on the spin and orbital motion of the conduction electrons, and the spin and orbital angular momentum l can then be used as good quantum numbers. We can then write δ^l for δ_j^l. In I it was shown, using the Golden rule, that the relaxation time T_1 is given by

$$1/T_1=(2\pi/\hbar)N_0c|\langle\beta|V_{\mathrm{so}}|\beta'\rangle|_{\mathrm{av}}^2\rho(E_F). \tag{4}$$

The states $|\beta\rangle$ are the one-electron states moving in the electric field of the lattice, and the symbol "av" means that the square of the matrix element is averaged over all $|\beta\rangle$ and $|\beta'\rangle$ at the Fermi surface. N_0 is the number of host atoms per cc, c is the fractional concentration of impurities, and $\rho(E_F)$ is the density of states for both spins at the Fermi surface. Note that the above expression is twice the usual expression obtained using the Born approximation[10]; this is because spins in both quantum states can flip.[21]

The relaxation time T_1 is related to the spin-flip scattering cross section per impurity, this being a more convenient way of expressing the results:

$$\sigma=1/N_0V_FcT_1, \tag{5}$$

where V_F is the velocity of an electron at E_F. Thus

$$\sigma=(2/\pi)[(m^*)^2/\hbar]|\langle\beta|V_{\mathrm{so}}|\beta'\rangle|_{\mathrm{av}}^2, \tag{6}$$

where m^* is the effective mass of the solvent material. If we write the spin-orbit coupling as

$$V_{\mathrm{so}}=\frac{\hbar^2}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\mathbf{l}\cdot\mathbf{s}, \tag{7}$$

where $\mathbf{l}$ and $\mathbf{s}$ are now measured in units of $\hbar$, then σ can be written in a form free of $\hbar$,

$$\sigma=\frac{2}{\pi}\left(\frac{m^*}{m}\frac{1}{2mc^2}\right)^2\sum_l\frac{l(l+1)}{3(2l+1)}\left|\left\langle\beta_l\left|\frac{1}{r}\frac{dV}{dr}\right|\beta_l'\right\rangle\right|^2, \tag{8}$$

where $|\beta_l\rangle$ is the wave function with angular momentum l.

$|\beta_l\rangle$ is found by matching the numerically integrated wave function to the wave function (2) at r_t. The matrix element in (8) is determined by differentiating the po-

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[18] W. A. Harrison, in *Phonons in Perfect Lattices and in Lattices with Point Imperfections*, edited by R. W. H. Stevenson (Oliver and Boyd, Edinburgh, 1966), p. 108.

[19] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[20] G. W. Pratt, Jr., Phys. Rev. **88**, 1217 (1952).

[21] C. P. Slichter, *Principles of Magnetic Resonance* (Harper & Row, Publishers, Inc., New York, 1963).

tential, multiplying by the square of the wave function, and integrating numerically using Simpson's rule. The results are shown, together with the phase shifts, in Table I. The contributions to the spin-flip cross section from the *d* part of the electron are negligible except where indicated.

In any column the agreement of the results with experiment is about the same, showing that the suggestion that the spin-flip relaxation is due to the spin-orbit coupling of the impurity is correct. The disagreement of theory with experiment occurs when the valence of the impurity varies. There are three points to notice:

(i) The theoretical values for the cross section due to the *p* character of the electron increase more rapidly than the experimental values as the valence difference increases from -1 to $+3$.

(ii) The theoretical values continue to increase when the valence difference changes from $+1$ to $+2$ to $+3$, while the experimental values always decrease when the valence difference goes from $+2$ to $+3$.

(iii) In *Li*Pd and *Li*Pt the theoretical *d* contribution is much larger than the *p* contribution and the experimental results. In the experiment, this large *d* contribution does not occur, and the reason for this may be the same as the reason for (ii).

We shall comment on the reasons for (i) and (ii) later.

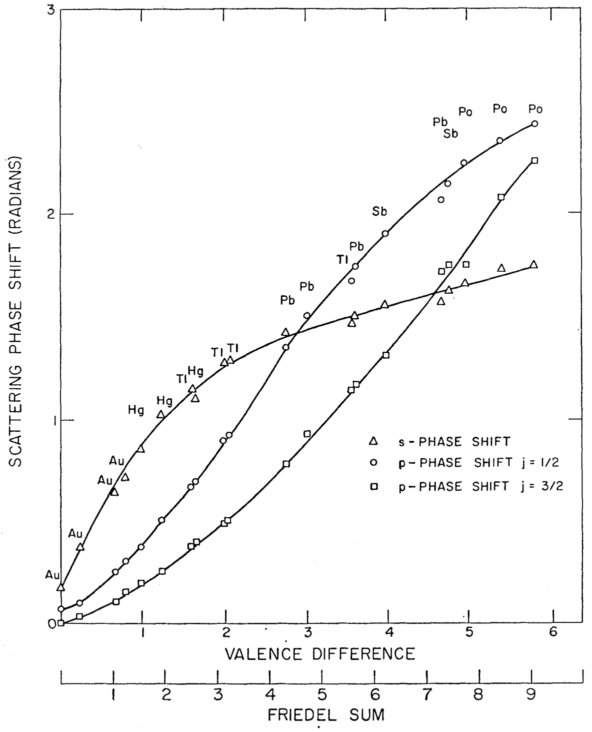

FIG. 2. Scattering phase shifts given by the model potential versus valence difference (or Friedel sum) using Herman-Skillman free-atom potentials of different free atoms in the gold row of the periodic table.

V. STRONG-COUPLING METHOD

The applicability of Fermi's "Golden rule" is limited to those cases where the probability of a transition is small; this required that the product of the strength of the perturbation and the time that the perturbation acts be small. The strength of the spin-orbit coupling increases as the impurity becomes heavier, and the time that the spin-orbit interaction acts will depend on the amplitude of the *p* part of the wave function at the impurity cell. This is likely to increase as the valence difference increases. Thus, it is possible[6] that perturbation theory may be invalid for heavy impurities with large valence differences.

The physical model presented here fixes the direction of the spin of the electron outside the unit cell of the impurity; but when the electron enters the impurity cell, the spin precesses because of its spin-orbit interaction due to the impurity. If the precession becomes large, the Born approximation is no longer valid. The cross section depends on the square of the sine of the angle of precession, so that the cross section will increase until this angle beomes $\frac{1}{2}\pi$, and then it will decrease if the angle becomes larger than $\frac{1}{2}\pi$. It is possible that the down turn in the experimental cross section is due to this effect, so that we have done calculations in which the spin-orbit coupling is taken into effect directly. These calculations give a down turn at valence difference between 3 and 4, larger than the experimental values. We shall argue from the experimental results that any falloff in this way is not due to such an effect.

In the strong-coupling scheme, the total angular momentum j is a constant of the motion, whereas the orbital angular momentum l and the spin angular momentum are not. j can have the two values [Eq. (1)], so that there are two phase shifts δ_j^l for each value of l.

Before the electron feels the impurity, it is supposed free, with its spin perfectly polarized, in the up-spin state, say,

$$\psi \sim \exp(i\mathbf{k}_F \cdot \mathbf{r})\alpha. \tag{9}$$

After scattering by the impurity, the wave function of the electron has both a scattered element with the same spin α and one with the opposite spin β,[22]

$$\psi \sim \{[\exp(i\mathbf{k}_F \cdot \mathbf{r}) + (1/r)f(\theta,\phi)\exp(ik_F r)]\alpha + (1/r)g(\theta,\phi)\exp(ik_F r)\beta\}. \tag{10}$$

For a spherically symmetric potential it can be shown[22,23] that

$$f(\theta,\phi) = (1/2ik_F)\sum_l \{(l+1)[\exp(2i\delta_{l+1/2}^{\,l}) - 1] + l[\exp(2i\delta_{l-1/2}^{\,l}) - 1]\}P_l(\cos\theta) \tag{11}$$

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[22] N. F. Mott and H. S. Massey, *The Theory of Atomic Collisions* (Oxford University Press, New York, 1949), 2nd ed.

[23] C. G. Darwin, Proc. Roy. Soc. (London) **A118**, 654 (1928).

TABLE III. Strong-coupling phase shifts and cross sections.

	Phase shifts					Cross sections (10^{-17} cm^2)	
	δ_0	$\delta_{3/2}^1$	$\delta_{1/2}^1$	$\delta_{5/2}^1$	$\delta_{3/2}^1$	p	d
*Li*Mg	0.569	0.302	0.306	0.018	0.018	2.9×10^{-3}	...
*Li*Al	1.098	0.654	0.662	0.02	0.02	1.65×10^{-2}	...
*Li*Zn	0.621	0.251	0.271	−0.004	−0.004	0.108	...
*Li*Ga	1.254	0.603	0.653	0.006	0.007	0.69	...
*Li*Pd	−0.106	−0.017	−0.001	−0.353	−0.165	0.17	17.2
*Li*Ag	0.074	0.035	0.067	−0.042	−0.038	0.293	0.004
*Li*Cd	0.704	0.284	0.356	−0.012	−0.01	1.43	...
*Li*In	1.068	0.636	0.778	0.004	0.006	5.57	...
*Li*Sn	1.284	1.048	1.256	0.015	0.016	11.85	...
*Li*Pt	−0.368	−0.107	−0.049	−0.232	−0.115	0.938	6.84
*Li*Au	0.138	0.013	0.113	−0.062	−0.046	2.75	0.13
*Li*Hg	0.723	0.245	0.461	−0.024	−0.017	12.71	...
*Li*Tl	1.081	0.567	0.999	−0.015	−0.009	48.61	...
*Li*Pb	1.24	0.969	1.474	0.01	0.00	64.81	...
*Na*Cd	0.920	0.217	0.268	−0.008	−0.007	0.51	...
*Na*In	1.298	0.572	0.717	−0.0005	0.005	4.0	...
*Na*Sn	1.504	0.981	1.232	0.005	0.006	12.1	...
*Na*Au	0.179	0.002	0.071	−0.056	−0.04	1.97	0.19
*Na*Hg	0.925	0.192	0.349	−0.017	−0.011	4.8	...
*Na*Tl	1.264	0.499	0.894	−0.006	−0.002	29.2	...
*Na*Pb	1.44	0.892	1.485	0.004	0.007	61.4	...

and

$$g(\theta,\phi)=(1/2ik_F)\sum_l\left[\exp(2i\delta_{l-1/2}{}^l)-\exp(2i\delta_{l+1/2}{}^l)\right]\times\sum_{m=+1}p_l{}^m(\cos\theta)e^{im\phi}. \quad (12)$$

The total spin-flip cross section is

$$\tfrac{2}{3}\int\int|g(\theta,\phi)|^2d\Omega=\frac{4\pi}{k_F{}^2}\sum_l\frac{2l(l+1)}{3(2l+1)}\sin^2\zeta_l, \quad (13)$$

where

$$\zeta_l=\delta_{l+1/2}{}^l-\delta_{l-1/2}{}^l, \quad (14)$$

and the $\frac{2}{3}$ factor in (13) comes from averaging over all possible initial and final vectors. Since the d contributions to the spin-flip cross section are usually small, ζ_1 can be considered as the angle of precession of the electron spin.

To get the cross section defined in (5), Eq. (13) must be multiplied by $(m^*/m)^2$. Comparing (13) and (8), it can be seen that, when ζ_l is small,

$$\zeta_l=\frac{k_F|\langle\beta_l|(1/r)dV/dr|\beta_l'\rangle|}{2\pi 2mc^2}. \quad (15)$$

From (13) it can be seen that if ζ_l becomes greater than $\frac{1}{2}\pi$, there is a decrease in the cross section, as we argued before. Suppose that this is the mechanism which causes the decrease in the experimental results; then it can be seen, assuming that only the $l=1$ term in (13) is important, that the maximum cross section is

$$(8\pi/k_F{}^2)(m^*/m)^2\times2/9, \quad (16)$$

which gives, for Li, $\sigma_{\max}=8.0\times10^{-16}$ cm², and for Na, $\sigma_{\max}=6.3\times10^{-16}$ cm². This maximum would occur in both the Ag and Au rows of the periodic table. The experimental results show, however, that the peak cross sections in the Ag and Au rows differ by a factor of 10. We must thus conclude that the mechanism that causes the turn down in the experimental results is not a breakdown of perturbation theory.

This can also be seen quantitatively from the perturbation-theory results. If the spin-orbit coupling is small, δ_l can be found from these; even for Pb, the angles obtained would not invalidate perturbation theory.

Nevertheless, we have considered it worthwhile to do the calculations using the strong-coupling scheme. The method is not only more accurate but also easier: Only phase shifts have to be measured, and there is no match-

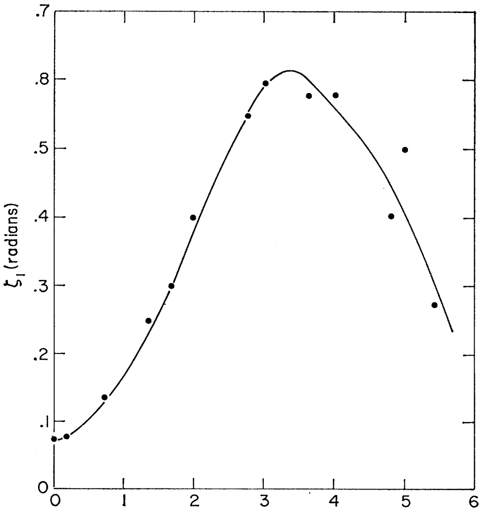

FIG. 3. ζ_1 versus valence difference for impurities in the gold row of the periodic table.

TABLE IV. Resistivities (in $\mu\Omega$ cm) per at.% of impurity.

	Calculations using phase shifts From Table I	From Table III	Experimental results	Ref.
*Li*Mg	1.06	1.04	0.83	a,b
			1.43	c
*Li*Al	4.08		4±1	a
*Li*In	4.31	4.42	8.6	a
*Li*Sn	7.54	8.66	1.0	b
*Na*Au	0.21	0.23	5	c
*Na*Cd	2.84	2.94	5	c
*Na*Tl	6.06	7.5	11	d
*Na*Sn	10.02	10.21	10.2	c
*Na*Pb	10.00	11.8	11.6	c

[a] D. K. C. MacDonald, W. B. Pearson, and I. M. Templeton, Phil. Mag. **6**, 1431 (1961).
[b] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **83**, 149 (1954).
[c] T. E. Faber, Phil. Mag. **15**, 1 (1967).
[d] J. F. Freeman and W. D. Robertson, J. Chem. Phys. **34**, 769 (1961).

ing of wave functions at r_t. ζ_l is given directly, and we are able to see how it varies with valence difference (see Figs. 2 and 3).

The methods used were as described in Secs. II and III, although in this case the spin-orbit coupling must be added to or subtracted from the atomic potential, depending on the vasue of j. The spin-orbit coupling had to be taken now as[24]

$$\alpha_s^2\frac{1}{r}\frac{dV}{dr}[2+\alpha_s^2V(r)] \tag{17}$$

to avoid having an attractive potential stronger than the centrifugal potential close to the impurity nucleus. α_s is Sommerfeld's fine-structure constant. No other relativistic terms have been added to the potential, since their importance when using a nonrelativistic potential is uncertain.[24,25]

The results, shown in Table III, agree well with the perturbation-theory results, except in the case of the heaviest elements, thallium and lead, where ζ_l is large enough for there to be a significant difference between ζ_l and $\sin\zeta_l$.

VI. RESISTIVITY CALCULATIONS

We have used the calculated phase shifts to calculate the resistivity per percentage of impurity for various impurities in lithium and sodium, where experimental measurements have been made. The formula for the resistivity is [26]

$$\frac{4\pi\hbar c}{e^2k_F}\sum_{l=1}^{a} l\sin^2(\delta_{l-1}-\delta_l)\,, \tag{18}$$

when the spin-orbit coupling is neglected and

$$\frac{4\pi\hbar c}{e^2k_F}\sum_{l=0}^{\infty}\frac{l+1}{(2l+1)(2l+3)}\Big[\sum_{j=l+1/2}^{l+3/2}\sum_{j'=l-1/2}^{l+1/2}(j+\tfrac{1}{2})(j'+\tfrac{1}{2})$$
$$\times\sin^2(\delta_j^{l+1}-\delta_{j'}^{l})+2l\sin^2\zeta_l-2l(l+2)\sin\zeta_l\sin\zeta_{l+1}$$
$$\times\cos(\delta_{l+1/2}^{l}+\delta_{l-1/2}^{l}-\delta_{l+1/2}^{l+1}-\delta_{l+}^{l+1})\Big]. \tag{19}$$

[Equation (19) is derived in Appendix B.] The results are shown in Table IV. The agreement between theory and experiment is exceedingly bad in *Li*Sn and *Na*Au. Including the spin-orbit interaction in the other cases does improve agreement, but not spectacularly. It does, however, distinguish between the resistivities of *Na*Sn and *Na*Pb, and in doing so, gives very good agreement with experiment.

VII. VARIATION OF PHASE SHIFTS WITH VALENCE DIFFERENCE

In Fig. 2 we have plotted δ_0, $\delta_{1/2}{}^1$, and $\delta_{3/2}{}^1$ against the Friedel sum. The potentials used were the Herman-Skillman potentials for the gold row of the periodic table with phase shifts evaluated at the Fermi energy of sodium. There are several interesting points to be noticed:

(i) By varying the constant A, different potentials could be used to derive the same Friedel sum. When this was done, the phase shifts obtained did not vary much from potential to potential. In part, this shows that the phase shifts are fairly insensitive to the shape of the potential in any particular row of the periodic table. In part, it results from the fact that adding one nuclear charge does not change the potential by a large percentage near the core of the atoms. The same effect is also seen in other periodic rows and in lithium, but the phase shifts do vary quite considerably between different *rows* of the periodic table and in different host metals.

(ii) Although the d-wave phase shifts are small, they have a large weighting factor $(2j+1)$ in the Friedel sum, which means that they should not be ignored when the sum rule is applied. This is particularly necessary when the impurity has the same valence as the host and a just-filled d shell, as can be seen from the behavior of gold in sodium. There the contribution of the d phase shift to the Friedel sum is greater in magnitude than that of either the s or p phase shifts.

(iii) As the Friedel sum increases, the s-wave phase shift δ_0 increases rapidly at first and then flattens out to a value about $\frac{1}{2}\pi$. The p-wave phase shifts $\delta_{1/2}{}^1$ and $\delta_{3/2}{}^1$ increase slowly when the Friedel sum is small, but soon increase rapidly, until they are both greater than δ_0 when the Friedel sum corresponds to a valence difference of about 5.

(iv) When the Friedel sum is small, ζ is small, but it increases monotonically until it reaches a maximum

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[24] M. A. Ball (to be published).
[25] M. Rotenberg, Phys. Rev. Letters **16**, 969 (1966).
[26] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, New York, 1964), 1st ed.

when the Friedel sum corresponds to a valence difference of about 4. Then it decreases monotonically.

The behavior expressed in (iii) agrees with the atomic screening hypothesis of Odle and Flynn.[11] The s-wave phase shift only reaches $\frac{1}{2}\pi$, suggesting that only one s electron can be added to the s electron already present in the conduction band. Extra screening has then to be done by the p electrons, and it is noticeable that the $\delta_{1/2}{}^1$ phase shift is also beginning to flatten out by the time the equivalent valence difference is 5, suggesting that the maximum p-wave phase shifts are π.

The idea of a resonance in the p-like electrons suggested by Ferrell and Prange[14] and more recently by Viswanathan and Rajagopal[27] is very similar to the idea of a virtual bound state[7] that has been postulated for d-like electrons within a conduction band. We showed in I how it conflicted with the atomic screening hypothesis. Result (iv) shows that the maximum amount of p-like electron density occurs at a valence difference of 4. From (15) we see that ζ_1 is proportional to the amount of p-like electron density at the Fermi surface, so that we expect σ to be a maximum at a valence difference of 4, in disagreement with the resonance hypothesis and experiment.

Figure 3 shows ζ_1 as a function of valence Z and as a function of the total amount of p-like screening. It has a resonancelike shape with a peak at $Z=5$, and is so broad that ζ_1 is still significant when the valence difference is 1 or 7. This is in agreement with the measurements of Vassel on the residual resistivities due to impurities in copper and aluminum. In his paper, the results for impurities are p-like and, where d-like screening occurs, show the above kind of behavior with valence difference, although in copper the d resonance is split either by spin-orbit coupling or by the crystal field.

The curve of ζ_1 against total p-electron screening is important because it is likely, from general considerations, to be independent of any screening mechanism discussed. Assuming this, the experimental results for $Z=4$ can only be explained in a free one-electron theory by requiring the total p-electron density to be *much greater* or *much less* than predicted by the atomic screening hypothesis.

Figure 2 is also of use in discussing the effects of dilatation of the lattice, which is caused by the core of the impurity being a different size than that of the host metal. The displacement of atoms radially outward falls off inversely with the square of the distance, so that for a sphere of large radius R centered on the impurity, there is a net volume displacement outwards through the surface of the sphere, which is independent of R. This means that there is a decrease in the total electronic charge contained within the sphere. Theoretically, this can thus be accounted for by making the Friedel sum equal to

$$Z-1-\delta V/\Omega, \qquad (20)$$

TABLE V. Effects of dilation. Two sets of phase shifts are given: BAS refers to this paper; TK refers to Titman and Kellington (Ref. 28).

	$\delta V/\Omega$		δ_0	δ_1	δ_2
*Li*Ag	−0.513	TK	0.314	0.164	
		BAS	0.375	0.187	−0.027
*Li*Mg	−0.050	TK	0.542	0.367	
		BAS	0.597	0.321	0.018
*Li*Cd	−0.393	TK	0.632	0.518	
		BAS	0.830	0.464	−0.011

where $\delta V/\Omega$ is the fractional change in the size of the cell occupied by the impurity.[28] If we knew $\delta V/\Omega$, instead of recalculating our phase shifts to accommodate (20), we could rely on the result (i) and construct graphs like Fig. 2 for each host metal and for each row of the periodic table. We could then read off the phase shifts for the relevant values of (20).

Unfortunately, the values of $\delta V/\Omega$ are not obtainable experimentally in most of our samples, since the impurity concentrations are very small, but Titman and Kellington[28] have obtained volume corrections for Mg, Cd, and Ag in Li. The corrected phase shifts are given in Table V, along with the phase shifts obtained by Titman and Kellington, by using the Friedel sum rule and the experimentas results for the change in the solvent Knight shift; however, they only considered s and p phase shifts.

Suppose we attempt to explain the down turn, at large valence differences, in the experimental cross sections by the dilatation of the lattice; then from Fig. 2, it can be seen that such a down turn could not happen unless (20) were of the order of 0 or 6. This would require an absurdly large volume change, showing that such an explanation is untenable. In *Li*Pb, for instance, there is probably very little volume change; the intermetallic compound *Li*Pb has the same lattice structure as lithium and an almost equal lattice constant, suggesting that a lead atom does not displace a metallic lithium lattice by very much.

VIII. CONCLUSION

To summarize, we have used a modified potential containing parameters which are adjusted to fit the data to calculate the scattering phase shifts. For valence differences of 1 or 2, these give a good account both of the magnitudes and the trends of three kinds of experimental data: spin-flip scattering cross section, Knight-shift data, and resistivity.

For larger valence differences (3 or 4) the resistivity calculations are good in Na-based alloys, but not very good in Li-based alloys. The spin-flip cross sections peak at the wrong valence difference.

Our model is tantamount to having the screening done by a surface charge at a suitably chosen radius, an assumption which is clearly nonphysical since charge

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[27] K. S. Viswanathan and A. K. Rajagopal (to be published).

[28] J. M. Titman and S. H. Kellington, Proc. Phys. Soc. (London) **90**, 499 (1967).

densities should not change drastically over distances much shorter than the wavelength of electrons at the Fermi energy. Moreover, the well-known oscillatory nature of the charge density plus the possibility of charging effects make it likely that the potential is not flat even at the nearest-neighbor positions.

What is desirable is to find a practical theoretical approach which would include these effects. If that were possible, a test of a more realistic one-electron potential would be possible.

On the other hand, it is conceivable that correlation effects among the electrons are important. In free atoms these effects give rise to Russell-Saunders couplings and Hund's rules. To some extent these effects are included in the Herman-Skillman potential, but if they are the principal cause of the early turn down, we would not expect them to be found in a treatment such as we have given.

APPENDIX A: PROOF OF THE FRIEDEL SUM RULE (3) IN THE STRONG-COUPLING CASE

The proof will only be sketched here, since it follows the proofs given in Refs. 8 and 4.

Consider an electron with energy E,

$$E=k^2/2m. \tag{A1}$$

Its wave function will be a sum of wave functions classified by j and l. The radial part $r\phi_j^l$ will satisfy

$$\frac{d^2\phi_j^l}{dr^2}+2\left(E-U_j-\frac{l(l+1)}{r^2}\right)\phi_j^l=0, \tag{A2}$$

where U_j is the impurity potential plus the relevant part of the spin-orbit coupling. If we normalize in a large sphere of radius R, then

$$\phi_j^l\to(1/2\pi R)^{1/2}\sin[kr+\delta_j^l(k)-\tfrac{1}{2}l\pi] \tag{A3}$$

as R becomes large. Then it can easily be shown that

$$\int_0^R dr\,(\phi_j^l)^2\to\frac{1}{4\pi R}\times\left(R+\frac{d\delta_j^l}{dk}-\frac{1}{2k}\sin 2(kR+\delta_j^l-\tfrac{1}{2}l\pi)\right). \tag{A4}$$

Having the impurity at the center of the sphere will change the electronic density at energy E within the sphere. Let this change be $\Delta\rho(k)$. Then

$$\frac{d\Delta\rho(k)}{dk}=\frac{1}{\pi}\sum_{j,l}(2j+1)\times\left(\frac{d\delta_j^l}{dk}-\frac{1}{k}\sin\delta_j^l\cos(2kR+\delta_j^l-l\pi)\right). \tag{A5}$$

If we neglect the small oscillating term, then (3) is obtained.

For metals like lithium, whose equivalent mass is not unity, Eq. (A1) should probably be modified. This would lead to the Friedel sum being multiplied by m^*. In our calculations this has not been done, which might account for the fact that the theoretical results for lithium are larger relative to the experimental results than the results for sodium.

Note that the oscillating term in (A5) is different from the oscillating term when spin-orbit coupling is neglected. This should, however, only slightly affect the theoretical calculations on the nuclear resonance intensities in dilute alloys because these depend on an average of all the phase shifts.[12]

APPENDIX B: PROOF OF THE RESISTIVITY FORMULA (19) IN THE STRONG-COUPLING CASE

If $\sigma(\theta)$ is the differential cross section, the resistivity is[26]

$$\frac{hck_E}{e^2}\int\sigma(\theta)(1-\cos\theta)d\Omega. \tag{B1}$$

Taking both spin-flip and non-spin-flip cross sections, we can write

$$\sigma(\theta)=|f(\theta,\phi)|^2+|g(\theta,\phi)|^2. \tag{B2}$$

After much manipulation, Eq. (19) is derived.