SPIN-FLIP SCATTERING OF CONDUCTION ELECTRONS FROM IMPURITIES*

Joseph R. Asik,† Michael A. Ball, and Charles P. Slichter

Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois

(Received 28 March 1966)

Impurities in metals[1] have been the subject of numerous studies,[2] both theoretical and experimental. They have been of interest to many-body theorists[3] because they provide a realization of the system of a positive charge in a Fermi sea. Experimental studies of such diverse phenomena as their effect on electrical resistivity,[4] and on the Knight shift[2,5] and nuclear resonance intensity,[2] have lent support to the theoretical ideas of Mott,[6] Friedel,[2] Blandin and Friedel,[7] Kohn and Vosko,[2] and many others on the screening. Magnetic impurities have also been extensively studied both theoretically[2] and experimentally.[2] In this Letter we report the results of a new type of experiment, measurement of the effect of impurities on the spin-orientation lifetime of conduction electrons.[8] We have measured directly the spin-flip scattering cross sections for Fermi electrons of 14 different nonmagnetic elemental impurities in metallic lithium and seven impurities in metallic sodium. For impurities whose valence is close to 1, we can account for the cross sections by a simple theory which considers as a perturbation the interaction of the conduction-electron spin with its orbital motion in the electric field of the impurity (spin-orbit coupling).[9] Since the spin-orbit interaction occurs well inside the ion core of the impurity, these measurements provide information about the $l > 0$ terms of the conduction-electron wave function in the vicinity of the impurity nucleus. For the high-Z elements of Group III or IV, the simple theory deviates from the results, in some cases by rather large amounts.

The large spin-orbit interaction characteristic of higher Z impurities enables them to produce easily measurable effects for concentrations as low as one atom in 10^7. As a result, we are able to observe the spin-flip scattering from numerous elements not ordinarily believed to form primary base alloys with Li or Na.[10] In some cases we have observed solubility limits. When no effect is observed, it is possible to estimate an upper bound of the solubility limit.

The existence of a nonvanishing spin-flip cross section implies that the lifetime of a spin in a given orientation is limited. That is, there is an impurity contribution to the spin-lattice relaxation rate.[11] This contribution can be observed by measuring the effect of various concentrations of added impurity on the linewidth of the conduction-electron-spin resonance (CESR), since T_1 (the spin-lattice relaxation time) equals T_2 (the transverse relaxation time).[12] Such studies are, therefore, only possible in materials for which the CESR can be observed.[13]

Our measurements were made at X band and primarily room temperature using a superheterodyne epr spectrometer[14] which was frequency locked to the sample cavity. Field modulation and a lock-in amplifier at 35 cps were also employed. The "local oscillator" of the superheterodyne was obtained by generating a 60-Mc/sec sideband[15] on a fraction of the klystron output power. The samples were small particles of approximately 20-μ mean diameter produced by doping bulk metal with impurity, melting the metal in mineral oil, and subjecting the molten alloy to 10 000-rpm agitation. For particle sizes such as ours, the absorption line shape shows the characteristic asymmetric shape analyzed by Dyson.[16] Since the linewidth of our undoped lithium (sodium) is 1 G (6 G), and since our apparatus has sufficient sensitivity to measure lines 250 G broad for Li alloys and 100 G for Na alloys, the extra broadening due to the impurities was readily measured.

Using the one-electron approximation and considering the spin-orbit interaction as a perturbation, one can easily find the equation for the impurity contribution[17] to the spin-lattice relaxation time,

$$\frac{1}{T_1}=\frac{2\pi}{\hbar}N_0 c\,|(\beta|V_{\mathrm{so}}|\beta')|_{\mathrm{av}}{}^2\rho(E_{\mathrm{F}}). \tag{1}$$

The states $|\beta)$ are the exact one-electron states of electrons moving in the electric field of the lattice and the impurity, but neglecting the spin-orbit interaction V_{SO} (with a single substitutional impurity). The symbol "av" means to average the square of the matrix

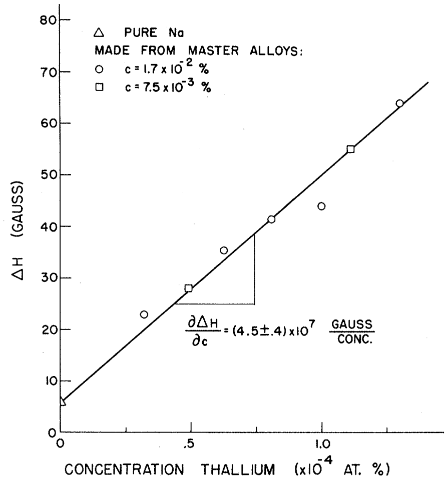

FIG. 1. The CESR linewidth ΔH in dilute sodium base alloys as a function of the thallium impurity concentration. The two independent master alloys were produced by direct doping. The samples were made by dilution of the master alloys.

element for both $|\beta\rangle$ and $|\beta'\rangle$ at the Fermi surface. N_0 is the number of host atoms per cm^3, c is the fractional concentration of impurity, and $\rho(E_F)$ is the density of states at the Fermi level E_F. We can relate the linewidth $\Delta H = 1.1/\gamma T_1$,[18] where γ is the electron magnetogyric ratio, to the spin-flip cross section σ by the equation

$$\sigma = \frac{\gamma}{1.1 N_0 v_F} \frac{\partial \Delta H}{\partial c}, \tag{2}$$

where v_F is the Fermi velocity.

To illustrate the basic data, Fig. 1 shows ΔH vs c for thallium in sodium. In Table I we give the experimental σ's for Ag and Au in Li and Au in Na. Since these substituents have the same valence as their hosts, no complications from screening of excess nuclear charge arise. However, it would not be appropriate to take the states $|\beta\rangle$ to be the well-known $|\vec{k}\rangle$ states of the pure metal, since the potential in the vicinity of the impurity atom is different from that of Li or Na despite the identity of valence.

Table I. Experimental and theoretical spin-flip scattering cross sections for monovalent impurities in lithium and sodium.

Alloy	σ_{exp} (cm^2)	σ_{theor} (cm^2)
LiAg	$(3.5 \pm 0.3) \times 10^{-18}$	9.1×10^{-18}
LiAu	$(6.8 \pm 1.0) \times 10^{-17}$	1.1×10^{-16}
NaAu	$(2.9 \pm 0.3) \times 10^{-17}$	3.5×10^{-17}

The simplest approximation for impurity atoms which produce large scattering compared with their hosts is to take the $|\beta\rangle$'s as plane-wave states orthogonalized to the impurity core states. As is well known, orthogonalization[19] (1) guarantees that the Pauli exclusion principle is satisfied and (2) produces atomiclike oscillations in the wave function in the vicinity of the nucleus. The resulting theoretical expression involves overlap integrals with core states (which we have evaluated numerically using the wave functions of Herman and Skillman[20]) and spin-orbit couplings of core states (obtainable experimentally from x-ray spectra[11]). The theoretical cross sections from this calculation (Table I) are seen to agree with experiment within a factor of 2.6 despite the fact that the experimental σ's cover a range of 20.

When the valence of the impurity differs from the host, the extra nuclear charge must be screened. Table II gives the experimental cross sections for nonmonovalent impurities. Since a single impurity adds a negligible total number of electrons to the band, the screening results from a change in the amplitude of the wave function of band electrons at the impurity, not a change in the number of occupied

Table II. Experimental and theoretical spin-flip scattering cross sections for impurities having a valence difference $V-1$ with respect to lithium and sodium.

Alloy	$V-1$	σ_{exp} (cm^2)	σ_{theor} (cm^2)
LiMg	+1	$(6.4 \pm 0.5) \times 10^{-21}$	2.7×10^{-21}
LiAl	+2	$(1.6 \pm 1.0) \times 10^{-20}$	1.5×10^{-20}
LiZn	+1	$(6.8 \pm 0.6) \times 10^{-19}$	2.9×10^{-19}
LiGa	+2	$(1.5 \pm 0.1) \times 10^{-18}$	1.6×10^{-18}
LiPd	−1	$(2.0 \pm 0.3) \times 10^{-18}$	2.4×10^{-18}
LiCd	+1	$(7.5 \pm 0.7) \times 10^{-18}$	1.9×10^{-17}
LiIn	+2	$(1.0 \pm 0.1) \times 10^{-17}$	5.2×10^{-17}
LiSn	+3	$(2.2 \pm 0.3) \times 10^{-18}$	4.0×10^{-16}
LiPt	−1	$(2.5 \pm 0.4) \times 10^{-17}$	2.0×10^{-17}
LiHg	+1	$(1.1 \pm 0.1) \times 10^{-16}$	2.6×10^{-16}
LiTl	+2	$(8.9 \pm 0.9) \times 10^{-17}$	6.8×10^{-16}
LiPb	+3	$(1.6 \pm 0.3) \times 10^{-17}$	3.0×10^{-15}
NaCd	+1	$(6.6 \pm 0.8) \times 10^{-18}$	6.6×10^{-18}
NaIn	+2	$(2.3 \pm 0.3) \times 10^{-17}$	2.0×10^{-17}
NaSn	+3	$(2.8 \pm 0.6) \times 10^{-18}$	2.2×10^{-16}
NaHg	+1	$(9.6 \pm 1.5) \times 10^{-17}$	8.5×10^{-17}
NaTl	+2	$(2.7 \pm 0.3) \times 10^{-16}$	2.5×10^{-16}
NaPb	+3	$(2.0 \pm 0.3) \times 10^{-16}$	1.9×10^{-15}

states. Thus, if the impurity has two valence electrons, there must be approximately a charge of two electrons in the impurity atomic cell. This implies that a typical band wave function is $\sqrt{2}$ bigger within the impurity cell. From Eq. (1) we see this will increase the linewidth by approximately $(\sqrt{2})^4 = 4$. Roughly we expect the valence difference to lead to a V^2 dependence, where V is the number of valence electrons of the impurity. To make these ideas more rigorous, we have numerically integrated the Schrödinger equation using a screened Coulomb potential[2,6] with its screening length adjusted to satisfy the Friedel sum rule,[2] keeping only the s-, p-, and d-wave phase shifts. The p-wave contribution is the most important for this potential (s waves have vanishing spin-orbit coupling). We have orthogonalized the resultant solutions to the cores, obtaining the theoretical values shown in Table II. For Pd and Pt (which present repulsive potentials) and the Group-I or -II elements, this simple procedure gives excellent account of the results, over a wide range of experimental values. This demonstrates convincingly that (1) the mechanism of spin flip is indeed spin-orbit coupling[21] and (2) there is a valence effect of the sort we have outlined.

The discrepancy with the Group-IV elements gives striking testimony to that fact that the simple theory has broken down. A similar though less marked effect is seen for the Group-III elements. Retaining perturbation theory, we have tried to resolve the difficulty by performing numerical integration of the s-, p-, and d-wave radial equations at E_F using the Herman-Skillman atomic potentials[20] for various impurities. The potentials are atomic inside a radius R and uniform outside; R was adjusted to satisfy the Friedel sum rule. The results are substantially the same as those found using orthogonalized screened Coulomb functions.

We can suggest three possible explanations for the discrepancy. (1) The one-electron, weak-collision approximation is correct, but to be self-consistent the screened potential may have substantially different radial dependence than the potentials we have so far considered. (2) Possibly a one-electron theory is inadequate for the high-valence atoms. Certainly in free atoms the exclusion principle is important in limiting the possible total spin and total orbital angular momentum. The large energy differences from the different L-S multiplets give rise, for example, to Hund's rules. It is natural to suppose that in the metal one should describe the impurity in terms of the lowest lying free-atom states. For a low valence, these are nearly one-electron states since there are many states compared to the electrons which occupy them. The deviations should be more marked for atoms with larger valence. (3) A third explanation is that perturbation theory is failing for impurities with large spin-orbit coupling and large valence difference. One way of seeing this is to consider the precession of a spin in the spin-orbit field of a free atom. If this precession occurs for a time necessary for a Fermi electron to cross an atomic cell (about 10^{-15} sec), the precession angle is not small.

It is possible to check the third hypothesis by additional calculations. The scattering problem is set up in the j, l representation[22] instead of the more usual l, s representation. The phase shifts are the η_l^j, described by quantum numbers j, l. The spin-flip cross section[22] is found to be

$$\sigma = \frac{4\pi}{k_F^{\,2}} \sum_{l=1}^{\infty} \frac{l(l+1)}{2l+1} \sin^2\left(\eta_l^{\,l+1/2} - \eta_l^{\,l-1/2}\right). \quad (3)$$

Since p-wave scattering predominates, Eq. (3) predicts $\sigma \cong 0$ if $\eta_1^{3/2} - \eta_1^{1/2} = \pi$. The j, l phase shifts must satisfy a Friedel sum rule appropriate to a spin-dependent interaction, which is easily shown to be

$$Z_v = \frac{1}{\pi} \sum_j (2j+1)\left(\eta_{j-\frac{1}{2}}^{\;j} + \eta_{j+\frac{1}{2}}^{\;j}\right), \quad (4)$$

where Z_v is the valence difference. Using atomic potentials and carrying out such calculations, we have not found significantly better agreement for the Group-IV impurities.

We wish to thank Professor C. P. Flynn for many interesting and useful discussions, Professor H. J. Stapleton for the use of sample preparation equipment, and E. K. Cornell for experimental assistance.

---

*This research was supported in part by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-1198, and by the National Science Foundation, Grant No. NSF GP700.

[†] National Science Foundation Cooperative Fellow, 1963-1964.

[1] The report of a recent conference on this subject is given in Metallic Solid Solutions, edited by J. Friedel and A. Guinier (W. A. Benjamin, Inc., New York, 1963).

[2] For a modern discussion of alloys and additional references, see C. Kittel, Quantum Theory of Solids (John Wiley & Sons, Inc., New York, 1963), Chap. 18.

[3] J. S. Langer and S. H. Vosko, J. Phys. Chem. Solids 12, 196 (1959). Also, see Kittel, Ref. 2, Chap. 6.

[4] For a recent review, see F. J. Blatt, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4.

[5] R. L. Odle and C. P. Flynn, to be published.

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

[7] A. Blandin and J. Friedel, J. Phys. Radium 21, 689 (1960).

[8] We are aware of two previous measurements: N. S. Garif'ianov and M. A. Starikov, Zh. Eksperim. i Teor. Fiz. 35, 798 (1958) [translation: Soviet Phys.–JETP 8, 553 (1959)]; G. D. Wignall, J. E. Enderby, C. E. W. Hahn, and J. M. Titman, Phil. Mag. 12, 433 (1965).

[9] For the role of spin-orbit coupling in CESR relaxation, see R. J. Elliott, Phys. Rev. 96, 266 (1954).

[10] See M. Hansen, The Constitution of Binary Alloys (McGraw-Hill Book Company, Inc., New York, 1958), 2nd ed.

[11] For a recent review of CESR spin-lattice relaxation, see Y. Yafet, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1963), Vol. 14.

[12] For the proof of this, see Yafet, Ref. 11, and also T. R. Carver and C. P. Slichter, Phys. Rev. 102, 975 (1956).

[13] CESR has been observed in the following metals: Li, Na, K, Rb, Cs, and Cu.

[14] The spectrometer was designed by Dr. C. H. Henry.

[15] J. L. Hall and R. T. Schumacher, Phys. Rev. 127, 1892 (1962).

[16] F. J. Dyson, Phys. Rev. 98, 349 (1955); also see G. Feher and A. F. Kip, Phys. Rev. 98, 337 (1955).

[17] For an elementary calculation of this contribution, see D. Pines and C. P. Slichter, Phys. Rev. 100, 1014 (1955).

[18] We have studied the effect of having a distribution of particle sizes on the relation between ΔH and T_1 using Dyson's theory and find that $\gamma \Delta H T_1 = 1.1$ holds to within ±10% for our particle distributions and linewidths.

[19] See, for example, J. M. Ziman, Principles of the Theory of Solids (Cambridge University Press, Cambridge, England, 1964).

[20] F. Herman and S. Skillman, Atomic Structure Calculations (Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[21] For the role of spin-orbit coupling and spin-flip scattering in the Knight shift in superconductors, see J. Appel, Phys. Rev. 139, A1536 (1965).

[22] N. F. Mott and H. S. W. Massey, The Theory of Atomic Collisions (Clarendon Press, Oxford, England, 1965), 3rd ed., p. 257.

M_A CENTERS IN ADDITIVELY COLORED KCl

Irwin Schneider

U. S. Naval Research Laboratory, Washington, D. C.

(Received 7 March 1966)

Strong evidence now exists that an F_A center is simply an F center with an impurity ion at a nearest-neighbor site.[1-4] While similarly perturbed centers involving F aggregates would likewise be expected, their existence has not been clearly demonstrated. The purpose of the present note is to report evidence in KCl of the simplest such association, an M center with a Na$^+$ ion neighbor, i.e., an M_A center.

The usual M center consists of two nearest-neighbor F centers along a ⟨110⟩ lattice direction.[5-6] Its main transition, the M band, lies on the low-energy side of the F band. Figure 1 shows the absorption in this spectral region for three crystals which differ primarily in their Na$^+$ concentration. Curve a shows the M band in an undoped crystal with a natural content of 0.003 mole% NaCl. Compared to this spectrum, curve b reveals a weak absorption at about 820 mμ in a crystal with 0.04 mole% NaCl. The relative size of this shoulder absorption increases for crystals with increasing NaCl content until it predominates. This is evidently the case for a crystal containing 0.35 mole% NaCl, as shown in curve c. Similarly, the size of the F_A band (at about 580 mμ) relative to that of the F band is very small for the crystal of Fig. 1, curve a, but is comparatively larger for crystals with increasing Na$^+$ concentration.

The M center has three symmetry axes along which its optical dipole moments lie. One is the ⟨110⟩ vacancy axis, which is the direction for the M band. The other two are the ⟨110⟩ and ⟨100⟩ directions perpendicular to this axis. M-center transitions with moments along these normally overlap the F band. A common pro-