Spin Relaxation of Conduction Electrons in Liquid Metal Alloys. I. Theory

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A theory of the spin-relaxation time of conduction electrons in liquid metal alloys, applicable over the whole range of alloy compositions, is proposed. The conduction electrons, coupled by the spin-orbit interaction to the host and the impurity ions, are described by plane waves orthogonalized to both the host and impurity core states. The ionic structure enters into the calculation through the alloy-structure factors commonly used in the theory of the resistivity. The effects of the electron-electron interaction are discussed, in particular the possibility of determining an upper bound for the exchange enhancement factor κ_0^2 is considered. An explicit formula for the calculation of the spin-relaxation time is given, together with an analysis of the approximations involved.

I. INTRODUCTION

The purpose of this paper is to propose a theory of the spin-relaxation time of conduction electrons in liquid metal alloys which is applicable over the whole range of alloy compositions.[1] It generalizes a theory[2] for pure metals which was recently used to interpret conduction-electron–spin-resonance (CESR) linewidth measurements in liquid sodium and liquid potassium.[3] The validity of previous theories is restricted to dilute alloys in which the spin-flip mechanism is dominated by the impurities.[4]

In Sec. II we discuss the model. The expression for the spin-relaxation time is derived in Sec. III. In Sec. IV we discuss the effect that the approximations involved in the model could have on the results. An account is also given of the enhancement effect of the electron-electron interaction on the spin-relaxation time, and the possibility of determining an upper bound for the exchange enhancement factor κ_0^2 is considered.

The application of this theory to interpret CESR linewidth measurements in liquid sodium-potassium alloys is presented in the following paper, hereafter referred to as II.

II. MODEL

In nonmagnetic liquid metals heavier than lithium, the main spin-flip mechanism is the spin-orbit interaction[5]

$$H_{so} = (1/2m^2c^2)\,\vec{s}\cdot \operatorname{grad} V \times \vec{p}\,, \tag{1}$$

where $\vec{s}$ and $\vec{p}$ are the electron spin and momentum operators, respectively. The potential V is approximated by a sum of spherically symmetric nonoverlapping potentials v^μ due to ions at positions $\vec{R}_\mu$. μ denotes the type of ion,

$$V(\vec{r}) = \sum_{\mu,\vec{R}_\mu} v^\mu(\vec{r}-\vec{R}_\mu)\,. \tag{2}$$

Then, the spin-orbit Hamiltonian becomes

$$H_{so} = \sum_{\mu,\vec{R}_\mu} \xi^\mu(\vec{r}-\vec{R}_\mu)\vec{s}\cdot\vec{L}_{\vec{R}_\mu}\,, \tag{3}$$

where

$$\xi^\mu(\vec{r}) = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dv^\mu}{dr}\,, \tag{4}$$

and $\vec{L}_{\vec{R}_\mu} = (\vec{r}-\vec{R}_\mu)\times\vec{p}$ is the angular momentum operator referred to the site $\vec{R}_\mu$.

The conduction-electron wave functions are approximated by orthogonalized plane waves (OPW)

$$|\vec{k}, s) = C_k^{-1/2}\Big(|\vec{k}, s\rangle - \sum_{\mu,\vec{R}_\mu}\sum_\lambda \langle\varphi_\lambda^\mu(\vec{r}-\vec{R}_\mu)|\vec{k}, s\rangle|\varphi_\lambda^\mu(\vec{r}-\vec{R}_\mu)\rangle\Big)\,, \tag{5}$$

that is, plane waves of momentum $\vec{k}$ and spin component s, $|\vec{k}, s\rangle$, which are made orthogonal to the core states of each ion at its site $\vec{R}_\mu$. $|\varphi_\lambda^\mu(\vec{r}-\vec{R}_\mu)\rangle$ denotes the core state with quantum numbers n, l, m, s (represented by λ) of the ion at the site $\vec{R}_\mu$. The normalization factor C_k is given by

$$C_k = 1 - N\textstyle\sum_\mu c_\mu \sum_n \sum_l \sum_m |\langle\varphi_{nlm}^\mu(r)|\vec{k}\rangle|^2\,. \tag{6}$$

c_μ denotes the atomic concentration of ions of type μ, and N the total number of ions contained in the volume $\mathcal{V}$.

In this problem it is essential to use the self-consistent ion potential $v^\mu(r)$, since the spin-orbit coupling occurs mainly inside the ion core. It would be wrong to start with plane waves and a pseudopotential as it is usually done in treating phenomena which involve electron scattering processes such as resistivity.

For computational purposes it is convenient to develop the plane wave in terms of spherical harmonics

$$|\vec{k}, s\rangle = \mathcal{V}^{-1/2} e^{i\vec{k}\cdot\vec{r}} |s\rangle = 4\pi \mathcal{V}^{-1/2} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(kr) \times Y_l^m(\nu, \varphi) Y_l^{-m}(\alpha, \beta) |s\rangle \ , \quad (7)$$

and to use core wave functions of the form

$$\varphi_{nlm}^{\mu}(\vec{r}) = R_{nl}^{\mu}(r) Y_l^m(\nu, \varphi) Y_l^{-m}(\alpha, \beta) |s\rangle \ ; \quad (8)$$

ν, φ and α, β are the angular coordinates of $\vec{r}$ and $\vec{k}$, respectively, referred to the spin quantization axis, and $j_l(x)$ are the spherical Bessel functions.

The electron-electron interaction is considered only through its screening effect on the ion potentials and its possible enhancement effect on the spin-relaxation time.

The ionic structure is described by means of the structure factors introduced by Faber and Ziman[6] in connection with the theory of the resistivity of liquid alloys.

In the first Born approximation the CESR relaxation time T_1 is given by[4]

$$\frac{1}{T_1} = 2\pi\rho(E_F) \iint \frac{d\Omega\, d\Omega'}{(4\pi)^2} \langle |(\vec{k}_F', \downarrow | H_{so} | \vec{k}_F, \uparrow)|^2 \rangle_T \ , \quad (9)$$

where $\rho(E_F) = mk_F/\pi^2$ is the free density of states at the Fermi level, including both spin orientations. $\langle \cdots \rangle_T$ indicates that a thermodynamical average over the positions of the ions has to be taken.

III. RELAXATION TIME

Replacing the OPW given by (5) in (9) and using (7) and (8) we obtain

$$\frac{1}{T_1} = \frac{2\pi}{\mathcal{V}} \rho(E_F) \iint \frac{d\Omega\, d\Omega'}{(4\pi)^2 C_{k_F}^2} \times \Big\langle \Big| 8\pi^2 \sum_{\mu, \vec{R}_\mu} \sum_{l} \sum_{m} s_l^{\mu} [(l-m)(l+m+1)]^{1/2} \times Y_l^{m+1}(\alpha', \beta') Y_l^{-m}(\alpha, \beta) e^{i(\vec{k}_F - \vec{k}_F')\cdot\vec{R}_\mu} \Big|^2 \Big\rangle_T \ , \quad (10)$$

where

$$s_l^{\mu} = A_l^{\mu} - 2T_l^{\mu} + D_l^{\mu} \ , \quad (11)$$

$$A_l^{\mu} = \int dr\, r^2 j_l^2(k_F r) \xi^{\mu}(r) \ , \quad (12)$$

$$T_l^{\mu} = \sum_n O^{\mu}(n, l) \int dr\, r^2 j_l(k_F r) \xi^{\mu}(r) R_{nl}^{\mu}(r) \ , \quad (13)$$

$$D_l^{\mu} = \sum_n \sum_{n'} O^{\mu}(n, l) O^{\mu}(n', l) \int dr\, r^2 R_{nl}^{\mu}(r) \xi^{\mu}(r) R_{n'l}^{\mu}(r) \ , \quad (14)$$

$$O^{\mu}(n, l) = \int dr\, r^2 j_l(k_F r) R_{nl}^{\mu}(r) \ . \quad (15)$$

The result (10) includes the assumption that there is no overlapping of core wave functions belonging to different atoms. A_l^{μ} represents the contribution to the spin relaxation coming from the plane-wave part of the OPW, and D_l^{μ} that coming from the core states. T_l^{μ} is an interference term. The contribution of the core amounts to about 90% of the effect. We limit the sums to the quantum numbers n, l, m, corresponding to occupied core states. In doing so, the contributions arising from the plane-wave terms A_l^{μ} of higher angular momentum are disregarded, but this introduces only a negligible error ($< 0.1\%$).

Equation (10) may also be written as

$$\frac{1}{T_1} = \frac{2\pi\rho(E_F)}{\mathcal{V} C_{k_F}^2} \iint \frac{d\Omega\, d\Omega'}{(4\pi)^2} (8\pi^2)^2 \times \sum_{\mu,\nu} \sum_{l,l'} \sum_{m,m'} (l, m)(l', m')^* \times s_l^{\mu} s_{l'}^{\nu} \Big\langle \sum_{\vec{R}_\mu} \sum_{\vec{R}_\nu} e^{i\vec{q}\cdot(\vec{R}_\mu - \vec{R}_\nu)} \Big\rangle_T \ , \quad (16)$$

with

$$(l, m) = [(l-m)(l+m+1)]^{1/2} Y_l^{m+1}(\alpha', \beta') Y_l^{-m}(\alpha, \beta)$$

and $\vec{q} = \vec{k}_F - \vec{k}_F'$. Acccrding to Faber and Ziman[6]

$$\Big\langle \sum_{\vec{R}_\mu} \sum_{\vec{R}_\nu} e^{i\vec{q}\cdot(\vec{R}_\mu - \vec{R}_\nu)} \Big\rangle_T = N\{c_\mu \delta_{\mu\nu} + c_\mu c_\nu [S_{\mu\nu}(q) - 1]\} \ , \quad (17)$$

where $S_{\mu\nu}(q)$ are the structure factors of the liquid metal alloy. They depend on α, β, α', and β' only through the combination

$$\cos\gamma = \cos\alpha \cos\alpha' + \sin\alpha \sin\alpha' \cos(\beta - \beta') \ . \quad (18)$$

Using the relations[7]

$$e^{i\varphi}\Big(\frac{\partial}{\partial\theta} + i\frac{\partial}{\partial\varphi}\cot\theta\Big) Y_l^m(\theta, \varphi) = [(l-m)(l+m+1)]^{1/2} Y_l^{m+1}(\theta, \varphi) \ ,$$

$$P_l^1(\cos\gamma) = -\sin\gamma \frac{dP_l(\cos\gamma)}{d(\cos\gamma)} \ ,$$

and the sum rule for spherical harmonics

$$\sum_{m=-l}^{l} Y_l^m(\alpha', \beta') Y_l^{-m}(\alpha, \beta) = \frac{2l+1}{4\pi} P_l(\cos\gamma) \ ,$$

where $P_l^1(x)$ are the modified Legendre polynomials, we have

$$\sum_{m,m'} (l, m)(l', m')^* = \frac{(2l+1)(2l'+1)}{(4\pi)^2} \frac{P_l^1(\cos\gamma') P_{l'}^1(\cos\gamma)}{\sin^2\gamma} \times \Big| e^{i\beta'} \Big(\frac{\partial}{\partial\alpha'} + i\frac{\partial}{\partial\beta'}\cot\alpha'\Big) \cos\gamma \Big|^2 \ .$$

After some algebra and a change of variables $d\Omega'$

$\equiv d\Omega_{\alpha',\beta'} \to d\Omega_{\gamma,\delta}$, we finally obtain

$$\frac{1}{T_1} = \frac{(2\pi)^3 \rho(E_F) d}{3C_{k_F}^2} \sum_{l,l'} (2l+1)(2l'+1) \times \int_{-1}^{1} dx\, P_l^1(x) P_{l'}^1(x) F_{ll'}(x) , \quad (19)$$

where

$$F_{ll'}(x) = \sum_{\mu,\nu} s_l^\mu s_{l'}^\nu \{ c_\mu \delta_{\mu\nu} + c_\mu c_\nu [S_{\mu\nu}(x) - 1] \} , \quad (20)$$

with $x = \cos\gamma$, $q = |\vec{k}_F - \vec{k}'_F| = 2k_F \sin(\frac{1}{2}\gamma)$. $d = N/\mathcal{V}$ is the density of ions.

T_1 depends on the temperature through the structure factors and the Fermi momentum k_F which changes with the density of ions.

In regard to future applications it is convenient to specialize Eq. (19) for a binary alloy such that the only core orbitals involved are those with $l = 1$. An example is the sodium-potassium alloy, in which case (19) reduces to

$$\frac{1}{T_1} = \frac{4(2\pi)^3 \rho(E_F) d}{C_{k_F}^2} [c(s_1^K)^2 + (1-c)(s_1^{Na})^2 + c^2 (s_1^K)^2 (S_{KK} - 1) + (1-c)^2 (s_1^{Na})^2 (S_{NaNa} - 1) + 2c(1-c) s_1^K s_1^{Na} (S_{KNa} - 1)] . \quad (21)$$

Here c is the atomic concentration of K in Na, and

$$S_{\mu\nu} = \tfrac{3}{4} \int_{-1}^{1} dx\, [P_1^1(x)]^2 S_{\mu\nu}(x) . \quad (22)$$

At temperatures $T \ll \bar{T}_F$, where $\bar{T}_F$ is defined in Ref. 8, the electron-electron interaction produces an enhancement of the Pauli susceptibility and the spin-relaxation time in the same proportion[9]

$$\chi_P = \frac{\chi_P^0}{\kappa_0^2} , \quad T_1^{eff} = \frac{T_1}{\kappa_0^2} , \quad (23)$$

where χ_P^0 and T_1 are the unenhanced Pauli susceptibility and spin-relaxation time, respectively, and $\kappa_0^2 \leq 1$ is the enhancement factor. For sodium $\kappa_0^{-2} \sim 1.5$.[10] The spin-relaxation time deduced from the CESR linewidth [T_1(measured)] must be identified with T_1^{eff}.

IV. DISCUSSION

The description of a conduction electron in a liquid metal alloy by a single OPW is certainly an approximation. In order to assess how good it is, we analyze the results of a similar approximation in solids. We hope that our conclusions can be extended, at least qualitatively, to liquids. The possibility of constructing better wave functions in solids as linear combinations of OPW, allows us to compare more precise results with those obtained with a single OPW. Existing calculations on the subject are concerned with the spin-orbit splitting of bands Δ and the comparison with its "atomic" counterpart ξ resulting from the use of a single OPW.[11,12] They show that $1 \lesssim \Delta/\xi \lesssim 1.5$ (Δ/ξ increases with the atomic number of the crystal constituent), indicating an enhancement of the spin-orbit interaction due to the crystal structure. Physically, the enhancement can be attributed to a contraction of the wave function in the core region of each atomic site. Since the relaxation frequency $1/T_1$ is proportional to the square of the spin-orbit interaction ($\sim \Delta^2$), we may conclude that *the use of a single* OPW *leads to overestimates of the spin-relaxation time*. According to rough estimates contained in Ref. 12, the correction should be negligible for sodium, but it may start to be important for potassium. For crystals of heavy atoms the correction may be of a factor 2.

The structure factors may, in principle, be determined experimentally although this is rather cumbersome, requiring several independent measurements of the structure (three for a binary alloy). It is possible, however, to approximate them using the rigid-sphere model for the liquid alloy, in which case the Percus-Yevick equation has an exact solution.[13] The adjustable parameters in that model can be determined from resistivity measurements in the same alloy.

The radial core wave functions $R_{nl}^\mu(r)$ and the self-consistent potentials $v^\mu(r)$ of the ions in the metal can be approximated by those of the free atom,[14] with an estimated error of less than 1%. This is a consequence of the fact that the spin-orbit interaction takes place mainly within the ion cores. In particular, numerical results obtained for pure sodium and potassium show that within 0.1%, T_1 is independent of the approximation used to screen the ionic potentials.

We may conclude from the above considerations that the value of T_1 given by this theory is an upper bound, because the use of a better electron wave function or the addition of other possible spin-flip mechanisms would only decrease the value of T_1. If, nevertheless, the calculated T_1 is still smaller than T_1 (measured), this can be attributed to the enhancement effect of the electron-electron interaction. In this sense the ratio T_1/T_1(measured) would provide an upper bound for the enhancement factor κ_0^2.

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Spin Relaxation of Conduction Electrons in Liquid Metal Alloys. II. Sodium-Potassium

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The results of conduction-electron–spin-resonance (CESR) measurements on liquid sodium-potassium alloys over the whole range of concentrations are presented. The experimental results are compared with the predictions of the theory proposed in Paper I, and with those of other theories which are valid in the low-concentration limit only. The possible errors introduced by using theoretical hard-sphere structure factors in the calculation are estimated. The relaxation time (RT) derived from the CESR linewidth exceeds the theoretical spin-lattice RT by a factor $\cong 1.85$ for all concentrations. This difference is attributed to the exchange enhancement of the conduction-electron spin lifetimes. An upper bound for the exchange-enhancement factor κ_0^2 is determined. The theory in I may also be used to calculate the contribution of vacancies to the spin relaxation of the pure metal. The results show that this effect is negligible at equilibrium vacancy concentrations.

I. INTRODUCTION

Conduction-electron spin resonance (CESR) in alloy systems has been little studied to date in either the solid or liquid phase. Most of the work reported has been involved with very dilute alloys of polyvalent impurities in monovalent hosts, the most extensive being that of Asik, Ball, and Slichter.[1,2] The work of these authors has been with lithium and sodium host metals in the solid phase and they have developed and applied two theories in an effort to explain their experimental results. As mentioned in the preceding paper[3] (henceforth I), these theories are only applicable to the dilute-alloy limit or what we may term the "initial-slope" behavior.

The results of Asik, Ball, and Slichter demonstrate the strong spin scattering produced by various heavy impurities in sodium and lithium, so large that only a fraction of one percent of impurity could be used before the resonance signal became unobservable above the detector noise in the system. To study an alloy system across the complete range of alloy concentration, one clearly requires alloys where the increased spin scattering produced by alloying is not negligible but is not sufficient to