PHYSICAL REVIEW B VOLUME 31, NUMBER 5 1 MARCH 1985

Spin-orbit relaxation and the Knight shift in small superconducting particles of simple polyvalent metals

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(Received 10 July 1984)

Recently it has been shown that the most efficient conduction-electron-spin relaxation mechanism in Al is associated with scattering events to and from certain portions (ridges) of the Fermi surface where the spin-orbit interaction leads to electron wave functions which have a substantial admixture of spin-up and spin-down components. Those ridges arise from intersections of the Fermi surface with Brillouin boundaries and therefore this relaxation mechanism must be common to and prevail in the simple (nontransition) polyvalent metals. Here, we show that in fact this mechanism accounts for the spin-flip processes responsible for the finite Knight shift observed in small Sn and Pb superconducting particles.

INTRODUCTION

The finite Knight shift observed in small superconducting particles[1–4] has been explained in terms of the surface spin-flip scattering of the conduction electrons mediated by the spin-orbit interaction.[5–7] The magnitude of this effect is customarily described by the parameter f, whose reciprocal, $1/f$, is the probability of spin-flip per surface collision. f has always been treated as an adjustable parameter.[1–8] Experiments on size-dependent residual Knight shift yield $f=8\pm1.5$ for tin[1] and $f=1.3-3$ for lead.[2] For aluminum $1/f$ is unmeasurably small[9] as expected for light metals.

Although the experimentally determined values of f were considered "reasonable", there was only one attempt, by Appel,[10] to actually obtain a theoretical estimate. In his model, the spin reversal is induced by the spin-orbit scattering of the conduction electrons at "displaced surface atoms".[10] It is difficult to extract quantitative predictions from Appel's model, nevertheless, at least in the case of Sn, it seems to yield spin-flip rates much smaller than the experimentally observed.

Recently, Silsbee and Beuneu[11] have shown that in aluminum, and most probably in all pure polyvalent metals, the conduction-electron spin relaxation is determined by certain portions (ridges) of the Fermi surface where the spin-orbit interaction is particularly effective in producing interband spin mixing. At those ridges the conduction-electron wave functions have a substantial admixture of both spin-up and spin-down components so that scattering processes to or from those ridges to the rest of the Fermi surface, where spin states are essentially pure up or pure down, lead to a randomization of spin *even* if the scattering potential is not spin dependent. In this paper we show that this spin-flip mechanism reproduces the values of f observed in Sn and Pb.

MODEL

The model of Silsbee and Beuneu[11] was introduced in connection with the problem of the temperature dependence of the electron-spin-resonance line width in Al. For electron-phonon scattering this model yields

$$\frac{1}{T_p}=\frac{C}{\tau_p}\,, \tag{1}$$

where $1/T_p$ is the phonon-induced spin-relaxation rate, $1/\tau_p$ is an average reciprocal lifetime of an electron on the Fermi surface, and C is a proportionality coefficient which in order of magnitude is given by

$$C=2\alpha\left[\frac{\lambda_v}{\Delta E}\right]^2\,, \tag{2}$$

where λ_v is the spin-orbit splitting parameter corresponding to the valence band, ΔE is the band gap at the ridge, and α is essentially the fraction of Fermi surface occupied by the ridges [Eq. (32) of Ref. 11].[12] The factor 2 in front accounts for the fact that spin flip can occur either on scattering to or from the ridges, which, for simplicity, are assumed to be randomly distributed on the Fermi surface. Calculations performed in the case of Al, as well as comparison with experiment, yield $C=1.5\times10^{-4}$. This model was also applied with success to the case of spin relaxation by dislocation scattering in cold worked Al.[13]

The basic ideas of this model should in principle apply to any polyvalent metal where the Fermi surface intersects Brillouin boundaries and for any scattering mechanism. Thus, in the case of the Knight shift of small superconducting particles of Al, Sn, or Pb, one should expect that a formula analogous to Eq. (1) holds, namely

$$\frac{1}{\tau_{\text{s.o.}}}=\frac{C_m}{\tau}\,, \tag{3}$$

TABLE I. Theoretical and experimental values of f (number of surface collisions per spin flip) and parameters used in the calculations.

Metal	Lattice parameter a (Å)	Fermi energy E_F (Ry)	λ_v (Ry)	$\vec{G}$	$\lvert\vec{G}\rvert$ (units of $2\pi/a$)	$U(\vec{G})$ (Ry)	N	$\alpha(\vec{G})$	$C(\vec{G})$	C_m	$f=1/C_m$	f(expt)
Sn				[200]	2.000	−0.11	4	0.58	1.15×10^{-2}			
	5.8	0.73	0.022	[101]	2.094	−0.06	8	0.58	3.88×10^{-2}	0.119	8.36	8 ± 1.5
	$(a/c=1.84)$			[220]	2.828	0.03	4	0.047	1.28×10^{-2}			(Ref. 1)
				[211]	2.896	0.02	16	0.093	5.63×10^{-2}			
Pb	4.90	0.702	0.0662	[111]	1.732	−0.0954	8	0.96	0.230	0.474	2.11	1.3–3
				[200]	2.000	−0.0482	6	0.26	0.244			(Ref. 2)
Al	4.04	0.856	6.7×10^{-4}	[111]	1.732	0.0179	8	0.12	8.4×10^{-5}	9.65×10^{-5}	10400	unmeasurably
				[200]	2.000	0.0562	6	0.018	1.25×10^{-5}			large (Ref. 9)

where $1/\tau_{\text{s.o.}}$ is the surface-induced spin-relaxation rate, $1/\tau$ is an average reciprocal electron lifetime due to surface scattering and C_m is a constant appropriate to each metal. We can approximate $1/\tau = V_F/l$, where V_F is the Fermi velocity and l is the particle diameter. Therefore,

$$C_m = \frac{l}{V_F\tau_{\text{s.o.}}} = \frac{l}{l_{\text{s.o.}}} \equiv \frac{1}{f} , \tag{4}$$

where $l_{\text{s.o.}} = V_F\tau_{\text{s.o.}}$ is the mean-free path for spin flip. C_m can be obtained from the band structure of the metal, and this was done for Al,[11,14] however, the calculation is rather cumbersome. For our purpose, an estimate of C_m should suffice.

The parameter λ_v in Eq. (2) has been calculated for several metals and a table is reported in Ref. 15. The values of ΔE and α will be estimated here on the basis of a nearly-free-electron model. Let us consider, in reciprocal space, a sphere centered at the origin and representing the Fermi surface of free electrons. Let there be another sphere with the same radius centered at $\vec{G}$, where $\vec{G}$ is a reciprocal-lattice vector. If $G < 2k_F$, where $G = \lvert\vec{G}\rvert$ and k_F is the Fermi wave vector, the two spheres intersect along a circle, and the band degeneracy along that circle is lifted by a small pseudopotential $U(\vec{G})$. It is straightforward to show that the gap obtained is

$$\Delta E = 2\,\lvert U(\vec{G})\rvert , \tag{5}$$

and that the "width" of the ridge (defined as the range of wave vector k for which the distance between the two nearly degenerate bands is within a factor of 2 from its minimum value ΔE on the ridge crest) is

$$\Delta k = \sqrt{3}\,\lvert U(\vec{G})\rvert /G , \tag{6}$$

where a.u. are used. The length L of the ridge generated by a reciprocal vector $\vec{G}$ is identified with the length of the circle of the intersecting spheres multiplied by a factor 2 to account for the two intersecting bands and by a factor N which is the number of equivalent $\vec{G}$ vectors; this gives

$$L = 2\pi N(4k_F^2 - G^2)^{1/2} . \tag{7}$$

Thus, the fraction $\alpha(\vec{G})$ of Fermi surface occupied by the ridges generated by $\vec{G}$ is

$$\alpha(\vec{G}) = \frac{\Delta k L}{4\pi k_F^2} , \tag{8}$$

and from Eq. (2) we obtain

$$C(\vec{G}) = \frac{\lambda_v^2 N\{3[4-(G/k_F)^2]\}^{1/2}}{4\,\lvert U(\vec{G})\rvert\, G k_F} . \tag{9}$$

Finally, C_m is given by a sum over all possible $(\lvert\vec{G}\rvert < 2k_F)$ types of ridges,

$$C_m = \sum_G C(\vec{G}) . \tag{10}$$

RESULTS AND DISCUSSION

The results for the parameter f of Sn, Pb, and Al are shown in Table I, together with the data used in the calculations. The band-structure information for Sn, Pb, and Al, was taken from Refs. 16, 17, and 18, respectively, and the corresponding values of λ_v were taken from Ref. 15, noticing that $\lambda_{nl}=2\Delta_{nl}/(2l+1)$, where Δ_{nl} is the tabulated spin-orbit splitting. To be consistent, this model must yield values of $\alpha(\vec{G})$ much smaller than 1; this is apparently not the case for some reciprocal vectors in Sn and Pb (Table I). We think, however, that the values close to 1 may easily result from the rough approximations involved in the calculations and not necessarily from an inadequacy of the model itself.

In former relaxation models it was assumed that the spin flip was caused by the spin-orbit part of the surface scattering potential and therefore, for an actual calculation, they required the details of the surface potential (for example, a knowledge of the displaced surface atoms,[10] or the shape of the surface barrier[19]). In this model, the surface simply provides a scattering mechanism (mostly spin independent) which randomizes the spin by connecting two states, one of which already contains spin admixture.

Surface scattering events involve large momentum transfer and therefore the errors introduced by the assumption of a random distribution of ridges on the Fermi surface (discussed in Ref. 13) is negligible in this case. A comparison of the value $C_{\mathrm{Al}}=9.65\times10^{-5}$ estimated here with that calculated in Ref. 11 (1.5×10^{-4}) indicates that our approximations are reasonable within a factor of 2. In this sense the excellent agreement displayed by the last two columns of Table I is not to be taken at face value. It shows, however, that the spin-flip mechanism proposed by Silsbee and Beuneu to account for the phonon-induced spin relaxation in Al, also explains the spin-orbit relaxation in small particles of simple polyvalent metals.

Finally, although the spin-orbit interaction is responsible for the spin relaxation in simple metals, the dominant acting mechanisms are quite different for polyvalent and for monovalent metals; therefore, it is only natural that a wide dispersion is found in trying to simply correlate the parameter f with the atomic number of the metal.[4]

ACKNOWLEDGMENTS

One of us (J.S.H.) wishes to acknowledge fruitful discussions with Dr. W. Baltensperger. He also acknowledges the partial financial support of the Fundacion Ricardo J. Zevada, the Organization of American States, the Consejo Nacional de Ciencia y Tecnología (Mexico)—National Science Foundation (CONACyT-NSF) Program and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq-Brazil).

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