Surface Relaxation Times of Conduction-Electron Spins in Superconductors and Normal Metals

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Electron spin relaxation times in surface collisions were deduced from measurements on superconductors of the NMR Knight shift, critical magnetic fields, and tunneling conductance as well as from measurements on normal metals by conduction-electron spin resonance. The relaxation times τ_{so} as determined by the various methods are consistent and depend on the atomic number of the metal in a manner similar to that proposed by Abrikosov and Gor'kov.

The spin relaxation time of conduction electrons in superconductors has been determined from NMR Knight-shift experiments,[1-6] from measurements of the critical field of ultrathin films,[7,8] and from spin-polarized tunneling experiments.[9] In normal metals, spin relaxation times have been determined from the linewidth of conduction-electron spin resonance (CESR). In each case the dominant relaxation mechanism is generally thought to be spin-orbit scattering. The purpose of this Letter is to show that where the mean free path is limited by surface collisions, the various types of measurements give spin relaxation times which, in their dependence on atomic number, are similar to that proposed by Abrikosov and Gor'kov (AG).[10]

The theory of superconductivity including spin-orbit effects is well understood. Particularly applicable to the present work on thin films are the reviews of Maki[11] and Fulde.[12] The AG theory was developed to explain Knight-shift results in superconductors. These authors calculated the probability of changing the electron spin direction in a collision with an impurity and suggested that the spin-orbit relaxation time τ_{so} should vary with the atomic number Z of the impurity approximately as

$$\epsilon \equiv \tau/\tau_{so} \approx (\alpha Z)^4. \quad (1)$$

Here ϵ is the probability that in a momentum-scattering collision there will be a change in spin direction. τ is the transport scattering time attributable to the impurity, $\alpha = e^2/\hbar c$, and Z is the atomic number of the impurity. To apply the theory to Knight-shift measurements of very thin films of pure metals, AG interpret τ as the surface collision time $\tau_s = d/V_F$, where d is the film thickness and V_F is the Fermi velocity. In this case Z is taken to be the atomic number of the pure superconductor.

In applying Eq. (1) to cryogenically condensed ultrathin films it was originally assumed[7,13] that the proper normalization would be obtained if τ was taken to be the measured transport relaxation time, τ. However, the resulting dependence of τ/τ_{so} on Z was much less than Z^4.[13] Furthermore, a recent study of ultrathin films of Ga has shown this normalization to be incorrect.[14] A Ga film about 100 Å thick was deposited on a substrate at 1 K and the value of τ_{so} was determined by a tunneling measurement before and after the amorphous film was annealed at 77 K to form a crystalline film. Even though the resistivity of the film decreased by a factor of 6, the value of τ_{so} as determined from tunneling measurements did not significantly change. Whatever scattering was associated with the additional resistance in the amorphous state was not effective in changing the spin direction and is meaningless in Eq. (1). At least for the annealed film, the best choice of normalization seemed to be to the surface scattering time. For the amorphous films the situation is more obscure, but the emphirical evidence still suggests that surface collisions dominate the spin scattering. Incidentally, Knight-shift experiments have been analyzed with the assumption of surface scattering because of the small characteristic dimension of the films or particles used.

In CESR for metals with cubic symmetry the spin relaxation time T_2 is equal to the spin-lattice relaxation time T_1,[15] and is obtained from the measured linewidth. Elliott[16] proposed that the spin-orbit interaction is the dominant mechanism of spin relaxation. It is usually assumed that T_2 in the absence of magnetic impurities can be written as $1/T_2 = 1/T_{ph} + 1/T_i + 1/T_s$ where T_{ph}, T_i, and T_s are the spin relaxation times from phonon, impurity, and surface collisions, respectively. For pure materials at low temperature

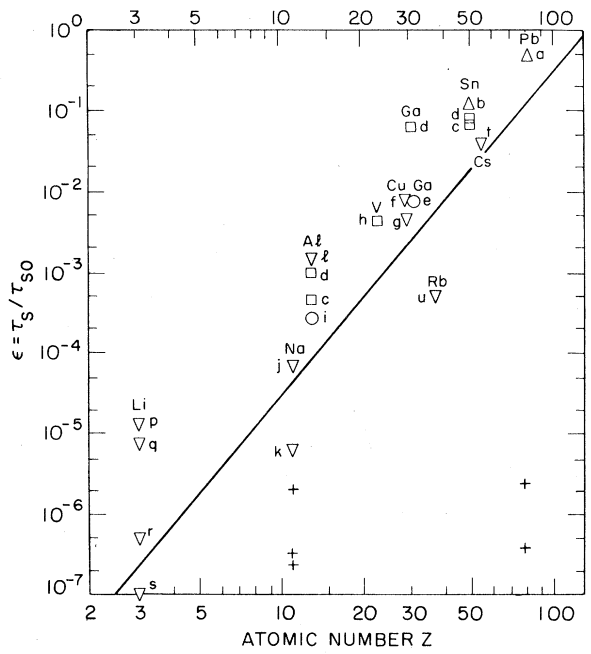

FIG. 1. The probability ϵ that a conduction electron will change its spin direction in a surface collision is plotted as a function of the atomic number Z of the metal. τ_s is the surface collision time and $\tau_{so}(=T_2)$ is the spin relaxation time in such collisions. The points shown were deduced from measurements on superconductors of the NMR Knight shift (△), critical magnetic fields of ultrathin films (□), and spin-polarized tunneling conductance (○), and from measurements on normal metals by CESR (▽). The solid line shows the Abrikosov-Gor'kov relation, $\epsilon = \tau_s/\tau_{so} = (\alpha Z)^4$, where $\alpha = e^2/\hbar c$. The points shown as + for Na and Au are for particles less than 100 Å in size and in the quantum size-effect region. Letters near the data points are coupled to the appropriate references numbers as follows: *a*, 1; *b*, 2 and 3; *c*, 13; *d*, 7; *e*, 14; *f*, 27; *g*, 25; *h*, 22; *i*, 9; *j*, last two works of Ref. 25; *k*, 30; *l*, 28; *p*, 31; *q*, 32; *r*, 34; *s*, 33; *t*, 26; *u*, 26.

the surface term can dominate. Dyson[17] gave a phenomenological treatment of CESR line broadening caused by spin relaxation and defined the probability ϵ of a spin disorientation during a surface collision by $1/T_s = \epsilon V_F/L$, where L is the characteristic dimension of the particle or film and V_F is the Fermi velocity. For a thin film we assume $L = d$; for a sphere of diameter D, Dyson gives $L = 2D/3$. Walker[18] has refined and extended Dyson's analysis of boundary scattering, but for the present survey where the values of ϵ often have large uncertainties, Dyson's simple expressions are used as they have been in most of the previously quoted values of ϵ. Thus $\epsilon = L/V_F\tau_{so}$, where we have made the identification $T_2 = \tau_{so}$.

Knight-shift measurements have been made on the elements Al,[4,5] Sn,[2,3] Pb,[1] Hg,[19] and V.[20] In small particles of Sn and Pb size-dependent Knight shifts were found which gave the values of ϵ which are shown (as triangles △) in Fig. 1. (In analyzing these experiments the characteristic surface-scattering distance for a sphere of diameter D was taken in the original work as $D/2$ and has not been changed.) The measurements on Al thin films showed that the Knight shift decreased greatly for $T \ll T_c$, and although no value was given for ϵ it is estimated to be less than 0.1. The earlier results on Hg were difficult to analyze quantitatively because of magnetic field effects. For V the Knight-shift measurements are completely dominated by orbital effects[21] so that they do not give the spin scattering times.

Critical-field measurements as a function of temperature have been made on films of Al,[7,8] Ga,[7] In,[13] V,[22] and Sn,[7,13] and are shown in Fig. 1 as squares. The spin-orbit scattering time was obtained from these measurements using the theory of Maki.[11] Tunneling measurements have been made on Al[9,13] and Ga[14] and analyzed by the theory of Engler and Fulde.[23] The results which were plotted in Ref. 13 using the normalization of the transport time determined from the resistance of $H_{c\perp}$ are now replotted in Fig. 1 (as circles) with L equal to the film thickness. Tunneling measurements have also been made[24] on Be[24] and τ_{so} was considerably longer than in Al, but no quantitative result for τ_{so} was obtained.

CESR measurements in which the linewidth is determined by surface scattering are in practice limited to a certain range of size and purity of the samples. In moderately heavy elements of extreme purity such as Cu, plates as thick as 10^{-2} cm can be studied at low temperature by the transmission method. For somewhat less pure materials, samples about 10^{-4} cm in size can be employed using the reflection method. For the light elements extremely pure samples whose size is less than 10^{-4} cm are required because the spin scattering rate is so small. However, for particles less than about 100 Å the finite separation of electron energy levels suppresses the spin-orbit scattering.[25] In this region [the quantum size-effect (QSE) region] the linewidth is expected to decrease inversely as the square of the particle size and be limited by effects other than spin-orbit scattering.

In Fig. 1 we plot (as inverted triangles ▽) CESR data in which surface scattering was demonstrated to be important and a value of ϵ could be deter-

mined. Results are given for Cs,[26] Rb,[26] Cu,[25,27] Al,[28] Na,[29,30] and Li,[31-34] but the results vary greatly in reliability. For most measurements on small particles the size and distribution of size was usually known only approximately. On the other hand, for measurements on plates of Cu and Na the size dependence was measured rather precisely. Also included in Fig. 1. (shown by crosses) are CESR measurements on Na[35-37] and Au[38,39] colloids whose size is 100 Å or less. These points are representative of the completely different pattern of results in the QSE region where spin-orbit scattering is suppressed.[40]

The conclusion that we reach from the data assembled in Fig. 1 is that a relation exists between ϵ and the atomic number Z which is roughly in accord with Abrikosov and Gor'kov as given by Eq. (1). Not only is ϵ approximately proportional to Z^4, but the absolute value is of the order of magnitude of $(\alpha Z)^4$. This result strongly supports the view that the conduction-electron spin scattering at a metal surface is caused by the spin-orbit interaction. This conclusion conflicts with calculations by Lisin and Khabibullin[41] who conclude that the spin-orbit interaction at a metal surface is much too weak to give the measured value of ϵ. The explanation of this disagreement may be that the jellium model assumed by these authors is not realistic enough. In this regard the agreement between the various types of measurements is important because in the case of superconductors the role of spin-orbit scattering has been documented in detail.

Having noted this general trend of the data, we next observe the severe dispersion of some of the measurements for individual elements. In this regard it should be emphasized here that most of the experiments claim no high precision. In presenting the data, we have kept the different values of L for a sphere used in the original work; uniformity in the choice of L would change some points but result in no overall change of pattern. In the superconducting experiments most of the results were obtained by assuming that only surface scattering was present and thus tend to give an upper limit on ϵ. Also in the case of CESR measurements on Li evaporated in argon (points p and q) we should probably consider the values of ϵ as upper limits because of the great reactivity of Li to oxygen which one expects to be present even in "pure" argon. With such widely divergent points as k (for Na) and u (for Rb) we have no explanation although they are single results in which the size may not have been exactly known. From a theoretical point of view there is no reason to expect the relation of Eq. (1) to be more than a first approximation which will be modified by the inclusion of other effects such as screening, many-body interactions, and surface conditions.

The present correlation of the data can serve several purposes. It should be useful in designing further experiments and choosing suitable sizes and materials so that higher-precision results can be obtained. It shows the usefulness of comparing data from the various sorts of measurements. It is hoped that this correlation will stimulate theorists to consider more carefully the nature of the spin-orbit interaction in metals and other complicating effects which must be considered in a detailed analysis of these experiments. For superconductors, spin scattering determines the behavior at high magnetic fields and is of technical importance.

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Effects of Uniaxial Stress on the Luminescence Lines Due to Multiexciton Complexes Bound to Phosphorus in Silicon

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We report the results of high-resolution studies of the effect of uniaxial stress on the bound-multiexciton–complex luminescence lines in phosphorus-doped silicon. Our results differ significantly from those contained in two previous studies which attempted to rule out the bound-multiexciton–complex explanation of these lines, and instead strongly support Kirczenow's shell model of the structure of the bound-multiexciton complexes. In addition, new lines are observed which are interpreted as stress-induced two-electron transitions of the bound exciton.

The bound-multiexciton–complex (BMEC) lines observed in the luminescence spectrum of lightly doped silicon have become the subject of considerable interest and controversy.[1-8] Kirczenow's[2] shell model (SM) of the structure of the BMEC has had considerable success in explaining the details of the luminescence spectrum. It also predicted the existence and behavior of several new lines which were subsequently observed.[3] An attempt to refute the SM by Sauer, Schmid, and Weber[4] (SSW) was answered by a critical comment[5] showing that most of the uniaxial-stress data presented by SSW actually supported the SM. A very similar interpretation of the effects of uniaxial stress on the BMEC spectrum has been given by Herbert, Dean, and Choyke.[6] Our results show that the one remaining problem raised in their publication, the lack of additional splitting of the β lines (we use the labeling scheme introduced by Kirczenow[2]) under $\langle 100 \rangle$ stress, is experimentally incorrect.

The high-stress studies of Sauer and Weber[7] (SW) of α^1 through α^4 posed another serious problem for *any* model based on BMEC. They claimed that while for low $\langle 111 \rangle$, $\langle 110 \rangle$, and $\langle 100 \rangle$ stresses the α lines showed identical doublet splittings, higher stresses resulted in additional fine structure in the lower-energy line of each of the α doublets. This behavior was rather puzzling, and no theoretical explanation of it was forthcoming, even for the simplest case, the α^1 bound exciton (BE) line. We have not been able to re-

