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Conduction-electron spin flip by phonons in metals: Analysis of experimental data

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We analyze the temperature-dependent part of the relaxation rate of conduction-electron spin in simple metals. According to the model of Elliott and Yafet the electron-spin-resonance (ESR) linewidth has the same temperature dependence as the resistivity. We have compared the experimentally measured ESR linewidth of Na, K, Rb, Cs, Cu, Ag, Au, Al, Be, and Mg by scaling it with the inverse of the square of the spin-orbit perturbation and plotting it versus reduced temperature, that is, T/T_{Debye}. A universal, Grüneisen-like curve is indeed followed by the monovalent metals, but large deviations appear in the cases of Al, Mg, and Be. The implications of these behaviors are discussed.

I. INTRODUCTION

When studying conduction-electron spin resonance (CESR) in pure metals, one is mainly concerned with two parameters: the position of the resonance line, that is to say the mean g factor of the conduction electrons, and the linewidth, corresponding to the spin-relaxation time. Since the work of Elliott[1] and Yafet[2] it is known that both quantities depend on the spin-orbit interaction.

On the other hand, a lot of experimental data concerning the g factor and the temperature dependence of the resonance linewidth are now available for metals corresponding to a wide range of spin-orbit potential strength. However, until now only very partial attempts have been made to compare these results between them. We find it particularly interesting to make such a comparison, because one can further test the validity of the model employed and then make predictions for the metals in which CESR has not yet been detected.

In this paper we are only concerned with conduction-electron spin relaxation in metals; the g-factor data will be studied elsewhere. We wish here to make a quantitative comparison of the behavior of the metals in which CESR has been detected up to now, concerning the variation of the spin-flip rate with temperature for these metals. In Sec. II we recall how a Grüneisen-type law is found for spin-flip scattering and we explain our way of reducing the data for different metals in such a manner that one should in principle obtain a "universal"—not metal-dependent—plot of linewidth versus temperature. In Sec. III we present the data reduction itself and in particular the experimental data used for this reduction. Finally we discuss the results of the comparison in Sec. IV.

II. GRÜNEISEN LAW FOR SPIN-FLIP SCATTERING

We recall the crucial steps of the calculation of conduction-electron spin flip by phonons as has been first proposed by Elliott[1] and Yafet.[2] The perturbation method followed is identical to that used for the classical calculation of the electrical resistivity of metals as a function of temperature, taking explicitly into account the effect of spin orbit both in the ion scattering potential and in the electron eigen wave functions.

The presence of the spin-orbit potential on each nucleus of the metal results in an eigenstate for the spin-wave function ($\Uparrow$ or $\Downarrow$), which is a mixture of $|+\rangle$ and $|-\rangle$ Zeeman states. The coefficient of admixture depends on the particular band structure and, in principle, can be calculated as a function of the wave-vector direction over the Fermi surface. In as much as the energy separation between the conduction band c and that issued from an atomic state i can be represented by a constant $\Delta E_i = E_c - E_i$ an order of magnitude of the spin-orbit admixture from that band is $\lambda_i/\Delta E_i$ where λ_i is the atomic spin-orbit splitting of the state i. The transition probability for spin-flip collisions of conduction electrons by phonons is calculated from the matrix element of the ion Coulomb and spin-orbit potential between the Kramers conjugate of spin-up and -down wave functions. The total spin-flip transition rate is then simply given by an integral of this matrix element over the phonons wave vectors weighted by the phonons density.[2]

The resulting temperature dependence for the spin-flip rate is linear for temperatures above the Debye temperature and varies like T^5 at low temperature. The similarity with the resistivity is striking. The identical linear dependence, at high temperature, of the resistivity and spin-flip rate is due to the fact that they are both determined by the number of available phonons. At low temperature the origin of this similarity lies in the same power dependence over the phonon wave vector involved in the integral although the matrix elements are different.

It is thus quite natural to compare the temperature dependence of the spin-flip rate obtained from the CESR linewidth as a function of temperature with the collision rate deduced from resistivity. Such studies have been carried out in detail on Na and K (Refs. 3 and 4) in solid or liquid form, and excellent agreement with Yafet's calculation was demonstrated in these two cases.

However, as new work on CESR of heavier metals appears it seems desirable to be able not only to link the spin-flip rate with the collision rate for a given metal, but also to relate the properties of different metals between them. This need stems mainly from two separate reasons, one practical, the other more physical. The first reason is that, because of the very rapid change of the spin-orbit strength with atomic number, the resulting broadening of the CESR linewidth is measurable only in the lowest temperature range for the heaviest metals (Cs, Au) whereas the higher temperature regime prevails for Na and K. In order to compare both cases, a simultaneous reduction of the data for a Grüneisen-like presentation is necessary. The second reason is as follows: The well-known Grüneisen plot brings together a large number of resistivity data from different metals.[5] This is a test of the validity of the Debye model and of the structure of the matrix element for electron-phonon collision. When spin-phonon collisions are considered, one more parameter is involved which is the average over the Fermi surface of the square of the spin-orbit admixture. If a similar "universal-type" behavior exists for the reduced values of CESR linewidth from different metals, it implies also an identity of those metals with respect to spin-orbit collisions. Such an analysis has been already done for Na and K (Ref. 4) quite convincingly. However, we will not follow exactly the same procedure. The usual way to reduce the resistivity data is to plot not the resistivity but the ratio of the resistivity at temperature T by that at T_D (T_D is the Debye temperature) versus T/T_D. In so doing one avoids all the trouble of estimating the factors involved in the amplitude of scattering and, of course, the resulting fit is impressive.[5]

In our case we want to test the validity of the estimate of the scaling factor, i.e., the spin-orbit admixture $\lambda/\Delta E$, and for this reason we do not want to force together all data by plotting a similar reduced ratio of linewidth at T divided by that at T_D. Instead we will only deal with the scaled linewidth that is $\Delta H(\lambda/\Delta E)^{-2}$. The resulting scatter may then have two origins: a large scatter due to misestimating the proper value of the spin-orbit perturbation and a smaller one inherent in the improper hypothesis that the scattering amplitudes are the same for different metals at a given value of T/T_D. We nevertheless hope (a) that this procedure can help to discriminate the behavior of the spin-flip scattering rates by phonons, and on the other hand (b) that this analysis can be reversed and used to predict the temperature dependence of the linewidth of metals for which no data exist.

III. DATA REDUCTION

The data of CESR linewidth are taken from Refs. 6–30 available in Table I for the following metals: Na, K, Rb, Cs, Be, Mg, Al, Cu, Ag, and Au. No attempt at this stage has been made to include linewidth data from the temperature dependence of CESR in semimetals like graphite[2], antimony[2], or Bismuth[2], or doped semiconductors in the metallic regime like Si-P or InSb; also, phonon relaxation of a ferromagnetic metal, although due to a very similar type of mechanism,[31] has been left out of the present analysis.[32,33] The linewidth measured experimentally is, like the resistivity, the sum of different contributions from impurities, defects, dislocations, surfaces, and phonons. In order to separate the temperature dependence of the linewidth, it is necessary to assume the equivalent of Matthiessen's law for spin scattering, that is, the independence of phonon scattering and impurity scattering.

In most available cases the validity of this assumption is shown by the lack of dependence of the temperature variation of the measured linewidth with sample origin, shape, and (nonmagnetic) impurity content. In some cases, particularly Mg and Be, a temperature-dependent linewidth increasing as the temperature decreases has been attributed to surface effects.[21,22] We have not attempted to resolve these questions and have only used the data in a temperature region where the phonon contribution appears dominant. In all the other cases only a substraction of a constant residual linewidth attributed to impurities and defects is involved, yielding possible largest errors at the lowest temperatures where the phonon contribution becomes small compared to the residual width. Special care must be taken with aluminum as it is now apparent that the CESR linewidth associated with phonons depends linearly on the measuring frequency.[27-30] Similar frequency-dependent spin-phonon collision might also exist for other metals like Mg or Be but no available data support this conjecture. In the case of Cu and Ag only a much smaller frequency dependence was observed.[27] As the vast majority of the data correspond to measurement at X band (9 GHz) we have used only experimental values at this frequency, in particular for Al.

The scaling parameter for the CESR-measured linewidth is $(\lambda/\Delta E)^{-2}$. Indicated in Table I is the atomic state from which λ is taken and the corresponding energy separation according to the values already quoted by Yafet.[2] It should be noted that λ is the spin-orbit splitting, not the spin-orbit constant, of that state.

Most often one state is evidently dominant for its contribution to the admixture coefficient among those quoted. As an example, the case of Cu is instructive: the conduction state is $4s$, the lowest excited state is $4p$ with spin-orbit admixture coefficient $(\lambda_{4p}/\Delta E_{4p-4s})^2 = 6.7\times10^{-5}$, for the highest filled p shell ($3p$) the coefficient is 1.38×10^{-3}, and for the highest filled d shell ($3d$) it is 2.16×10^{-2} and is reported in Table I. As noted in the discussion, one shortcoming of this type of evaluation for the spin-orbit perturbation amplitude is that one takes atomic level parameters whereas band structure should be considered. Nevertheless, when the bands considered are sufficiently far away in energy, one may think that the order of magnitude is still meaningful. A distinction has been necessary in the evaluation of the scaling parameter depending on whether the conduction electrons originate from an s state or contain p or d orbitals. In the case of an s band the p or d state immediately below contributes mostly as appears in Table I (except for Li and Be, of course). For s-p metals like Al, we define the spin-orbit admixture coefficient as the ratio of the spin-orbit splitting of the atomic valence p state by the Fermi energy evaluated in a free electron model. It turns out that in that case also

TABLE I. Parameters used for reduction of the experimental CESR linewidth versus temperature data. The main spin-orbit state is that which produces the largest spin-orbit perturbation $(\lambda/\Delta E)$ in the valence state considered. ΔE is the energy separation between these states and λ is the p or d spin-orbit splitting in the main spin-orbit state [see Yafet (Ref. 2)]. In the case of Pd the linewidth data used for Fig. 1 are taken from an analysis of *Pd*Mn dilute alloys made by G. Alquié [thesis, Université Paris, 1977 (unpublished)] and G. Alquié (to be published). The reducing parameter (not listed above) is the ratio of the spin-orbit splitting of the atomic $4d$ state by the width of the $4d$ band in Pd metal [see P. Lenglart, J. Phys. Chem. Solids 28, 2011 (1967)] and its square is evaluated at 5.3×10^{-3}.

Metal	Valence state	Main spin-orbit state	$(\lambda/\Delta E)^2$	T_D (K)	Refs.
Li	$2s$	$2p$	2.17×10^{-10}	360	6–9[a]
Na	$3s$	$2p$	2.73×10^{-5}	150	3,4,10–13
K	$4s$	$3p$	2.06×10^{-4}	100	14–16
Rb	$5s$	$4p$	3.16×10^{-3}	58	17–19
Cs	$6s$	$5p$	1.91×10^{-2}	42	17–19
Be	$2s$	$2p$	4.97×10^{-9}	1000	20–21
Mg	$3s$	$2p$	1.32×10^{-5}	290	22[a]
Ca	$4s$	$3p$	2.01×10^{-4}	230	23
Sr	$5s$	$4p$	3.02×10^{-3}	171	
Ba	$6s$	$5p$	1×10^{-2}	113	
Cu	$4s$	$3d$	2.16×10^{-2}	315	24,25
Zn	$4s$	$3d$	2.05×10^{-3}	200	
Ag	$5s$	$4d$	2.21×10^{-2}	215	24
Cd	$5s$	$4d$	6.78×10^{-3}	172	
Au	$6s$	$5d$	0.80	170	26
Hg	$6s$	$5d$	0.10	96	
Al	$3s$-$3p$	$2p$	3×10^{-5}	390	27–30
Ga	$4s$-$4p$	$3p$	9.6×10^{-4}	125	
In	$5s$-$5p$	$4p$	1.1×10^{-2}	106	
Sn	$5s$-$5p$	$4p$	9.3×10^{-2}	260	
Pb	$6s$-$6p$	$5p$	4.9×10^{-2}	88	

[a] See Note added in proof.

the highest filled p state below the s-p valence state is predominant in the spin-orbit perturbation.

Finally, the Debye temperatures used for the temperature scale have been taken from the standard determination from specific heat or resistivity.[34]

IV. DISCUSSION

In Fig. 1 the available published and unpublished CESR linewidth data, scaled according to the prescription of Table I, have been displayed versus reduced temperature T/T_D on a log-log plot. The experimental points have been omitted for sake of clarity and the temperature dependence of the CESR linewidth of each metal is depicted by a continuous line (within the temperature range of measurement) as an average of experimental points. It is possible to retrieve the original averaged value of linewidth at a given temperature by using the proper scaling parameters displayed on Table I. The dashed line is the graph of the Grüneisen function[34] which has been included, at an arbitrary ordinate, as a visual guide among the data.

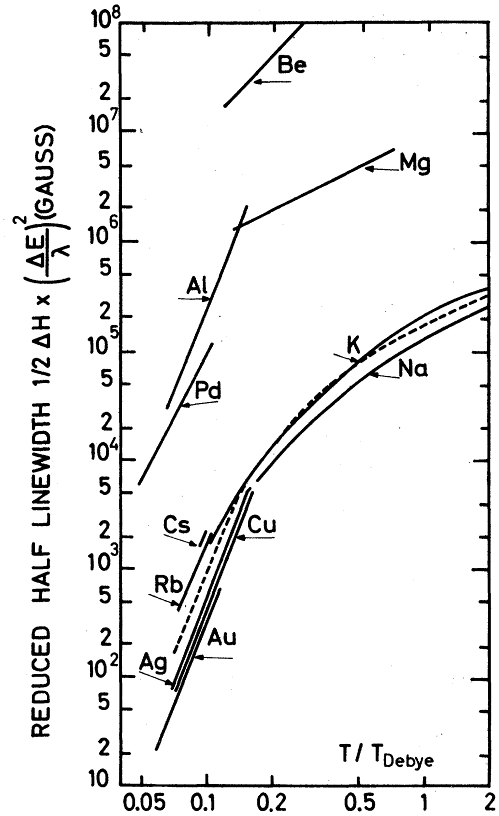

FIG. 1. Reduced linewidth vs reduced temperature for metals listed in Table I for which CESR data versus temperature has been found. The reducing parameter is the spin-orbit perturbation amplitude squared. The spin-flip scattering rate T_2^{-1} is obtained from the reduced half-linewidth $\frac{1}{2}\ \Delta H(\lambda/\Delta E)^{-2}$ by multiplying the value displayed by the coefficient listed in Table I and by $1.76 \times 10^7\ \mathrm{G}^{-1}\ \mathrm{sec}^{-1}$. The dashed line is the Grüneisen function set at an arbitrary ordinate for comparison.

It is immediately apparent that a large fraction of the metals considered fall closely together on this graph. This is quite encouraging as a justification for the very simplified reducing scheme used for the data. Furthermore, those metals which are grouped along the Grüneisen curve are precisely those for which the simple theory is supposed to work best, namely, the alkalis and the noble metals. We conclude that this allows to determine a "universal" quantity which is the *minimum* amount of spin-flip scattering by an ideal metal at a given value of T/T_D. Indeed, as the average performed over the Fermi surface concerns the *square* of spin-orbit perturbation, taking the maximum energy gap leads to a minimum estimate of the spin-flip scattering amplitude. The fact that for Al, Mg, and Be the reduced linewidths fall at least three orders of magnitude higher than the common set determined by the s-state metals is very instructive: this tells us that the energy denominator used for estimating the spin-orbit perturbation is overestimated (assuming the spin-orbit constant to remain at the atomic value). This implies that particular points should be sought in the band structure of these metals, where the energy separation between bands connected by spin-orbit perturbation is small. In the case of Al the electrons involved have been shown[35] to be near points K and W in the standard notation of the fcc zone mapping[36] and they belong to the third-zone pockets. For Mg and Be, which are hexagonal, the points involved are very likely the small needles near point K.[37] This type of analysis points to the essential inhomogeneous character of spin scattering of electron depending on their position on the Fermi surface.

The results from Fig. 1 can be used to predict the temperature-dependent linewidths of certain metals. An obvious and hitherto unobserved case is that of the temperature-dependent linewidth of Li. From Table I and Fig. 1, assuming the reduced linewidth of Li to follow the common set of the other monovalent metals, one predicts the linewidth of Li due to spin-phonon collision, at the melting point of Li (180 °C) to be about 0.1 mG (i.e., $T_2 \sim 0.5$ msec). Several other predictions concerning metals like Zn or In can be made and the failure to date to observe CESR down to He temperature on these metals strongly suggests that the very large deviations noted for Al, Mg, and Be are in fact a common feature associated with particular band-structure effects. Finally, and more tentatively, one can use the concept of minimum spin-flip scattering to check whether some reported observation of CESR on metals at finite temperature are consistent or not with all other available data included in Fig. 1 and thus may help to discriminate the possible origin of an observed resonance.[37]

As a last application one can use the collected results in Fig. 1 to estimate the possible effect of dislocations on the CESR of a metal. Indeed, the determination of the spin-flip cross section of a dislocation in Cu, Ag, and Al (Ref. 38) has shown the close similarity between spin flip by static defects and by phonons, provided both generate the same resistivity. Thus it is possible by a crude estimate of the phonon contributions to the spin-flip scattering to guess what is the maximum resistivity (induced by cold working), which is compatible with an acceptable broadening of the residual linewidth of a metal.

In conclusion we think that a systematic presentation and analysis of CESR linewidth of metals due to spin-phonon collision as is proposed here can help to understand the particular dynamics of more or less free electrons.[39]

Note added in proof. F. G. Cherkasov *et al.* have published recently [Phys. Lett. A 63, 339 (1977)] an investigation of ultrapure Li metal by electron spin echo method, thus avoiding in principle the inhomogeneous contribution to the CESR linewidth. Their data concerning the temperature dependence of lithium CESR shows a variation from about 10 mG at 77 K to 35 mG at the melting point of Li (460 K) with a possible residual width of 6 mG. These data points would appear in our Fig. 1 as a straight line with slope one passing through the point $[T/T_D = 1, \frac{1}{2}\Delta H(\Delta E/\lambda)^2 = 10^8]$. Such a widely different behavior of Li CESR linewidth when compared to all other alkalis and noble metals strongly suggests that a different, much more effective mechanism for relaxation takes place. Indeed the Overhauser mechanism [A. W. Overhauser, Phys. Rev. 89, 689 (1953)] seems adequate to account for the order of magnitude of the observed effect. It should be noted that this mechanism does not depend on atomic number, as does the spin orbit effect, but only on electron density. Thus it seems that Li would remain the only likely candidate for its study. Concerning recent measurement on Mg by R. P. Notley, J. R. Sambles, and J. E. Cousins [Solid State Commun. (to be published) it should be noted that the very improved data and analysis would shift the Mg line on Fig. 1 upward by a factor of about 3 confirming the anomalous behavior already observed.

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