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SMALL METAL PARTICLES: COMPLEMENTARY ASPECTS OF THE N.M.R. AND C.E.S.R. EXPERIMENTS (*)

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Résumé. — Durant cette conférence, nous désirons résumer les principaux résultats expérimentaux concernant la résonance magnétique dans les petites particules. Le couplage spin-orbite dans un métal est à l'origine du shift de g et, par conséquent, du temps de relaxation et du paramètre \( h/\tau \Delta \) que j'appellerai spin depairing parameter. (\( \Delta \) est l'écart moyen entre les niveaux électroniques et \( \tau \) le temps de relaxation de spin.) Ce paramètre, \( h/\tau \Delta \), est celui dont dépend le type de statistique qu'il faut appliquer au système de petites particules. C'est aussi de ce paramètre que dépendent la susceptibilité des particules paires dans l'état fondamental et la largeur de la raie de résonance des électrons de conduction lorsque le mécanisme de relaxation de spin est bloqué. Dans ce dernier cas, on s'attends pour les métaux purs à un élargissement prédominant dû au couplage hyperfin.

L'interaction des spins des électrons de conduction avec les spins de la matrice à la surface des particules provoque un élargissement de la raie C.E.S.R. Le shift de la raie R.M.N. dû aux électrons de conduction est le reflet, dans les particules paires, de l'interaction hyperfine électron-noyau et donc du facteur spin depairing. La largeur de la raie R.M.N. est en général dominée par les interactions avec les impuretés de la matrice comme la largeur C.E.S.R.

Une mesure indirecte du temps de relaxation de spin peut être obtenue à partir du facteur spin depairing lui-même mesuré à partir du shift résiduel de la raie R.M.N.

Abstract. — We summarize the main features and results of the magnetic resonance experiments on small particles. The spin-orbit coupling in the metal determines the electronic \( g \)-shift and hence the electron spin relaxation time and the spin depairing parameter, \( h/\tau \Delta \), where \( \tau \) is the spin relaxation time and \( \Delta \) is the average electronic level spacing. The depairing parameter governs the applicable statistics for the small particle system; the electronic susceptibility in even particles in the ground state; and the width of C.E.S.R. line when the spin relaxation mechanism is quenched. In the last circumstance the hyperfine broadening should be predominant in pure metals. Interaction of the conduction electron spins with spins in the embedding matrix at the particle surfaces produces broadening of the C.E.S.R. The N.M.R. shift in even particles reflects the electron nuclear hyperfine interaction and the electronic susceptibility, and hence the depairing parameter. The N.M.R. width is usually dominated by interactions with matrix impurities in analogy to the C.E.S.R. width. Values of the depairing parameter derived from residual N.M.R. shift give an indirect measurement of electron spin relaxation time.

1. Introduction. — Since the original calculations of Kubo [1] outlined the interesting properties of small particles, a number of theoretical [2-5] and experimental [6-11] studies have elaborated on the idea. The quantum size effects arise when the average energy level spacing \( \Delta \) in the particles satisfies the condition \( \Delta \approx kT \). At low temperatures the spin pairing in even particles tends to reduce their magnetic susceptibility, as may be observed in nuclear magnetic resonance (N.M.R.) experiments. The odd particles of monovalent metals contain a single unpaired spin which is paramagnetic and which may be observed by N.M.R., by conduction electron spin resonance (C.E.S.R.), or by conventional magnetic susceptibility experiments. The electron spin relaxation time is governed by spin-orbit coupling [12]. The spin-orbit coupling parameter also governs the mixing of electronic states so that the ground state of even particles is not purely singlet, which results in a residual Pauli paramagnetism [5, 11] at the lowest temperatures. In the magnetic resonance experiments the surface/volume effects are caused by paramagnetic impurities in the embedding matrix which couple to the conduction electron wave function. Broadenings of both C.E.S.R. and N.M.R. are attributable to the resulting spin density oscillations [13]. The N.M.R. and C.E.S.R. experiments are in many respects complementary, because of the hyperfine interactions. For example, the average electron spin polarization is measured by the N.M.R. shift in even particles, while the itinerant electrons sample effective fields of the nuclear spins and can show a hyperfine broadened line.

2. The conduction electron spin resonance. — The C.E.S.R. occurs at the frequency

\[ \omega_c = g\mu_B H/h \]

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in the applied field $H$, where the observed $g$-factor is shifted from the free electron value by 
$\Delta g = g - g_f$ resulting in a corresponding resonance shift $\Delta g/g$ which identifies the metal in question. The $g$-shift is related to the spin-orbit coupling [12] constant $\lambda$ and an appropriate energy band gap in the metal,

$$\Delta g \sim \lambda / \Delta E,$$  \hspace{1cm} (2)

and is generally small compared to unity. If $\Delta g$ is anisotropic or varies with position within a metal, the C.E.S.R. line may be broadened in proportion to this variation ($\Delta g$), unless line narrowing results from a short relaxation time [14]. The principal spin relaxation process at low temperatures arises from the spin-orbit coupling and may be estimated from the relation of Elliott,

$$1/\tau \approx v_F \Delta g^2 / d,$$  \hspace{1cm} (3)

where $v_F$ is the Fermi velocity and $d$ the particle diameter. This spin relaxation time provides an important contribution to the linewidth until the particle size is reduced below the limit where the parameter $\rho$ is of order unity,

$$\rho \sim \hbar / \tau \Delta.$$  \hspace{1cm} (4)

In this quantum size effect regime $\tau$ no longer retains the same meaning as a relaxation time [2], but rather becomes a parameter reflecting the size of the spin-orbit coupling. The average level spacing for the small particle is

$$\Delta = 4 E_F / 3 N,$$  \hspace{1cm} (5)

with $N$ equal to the number of conduction electrons in the small particle and $E_F$ the Fermi energy. Introducing the Fermi wave vector $k_F$ and metallic cell radius $r_s$ we have

$$\rho = 3 N^{1/3} \Delta g^2 / 4 r_s k_F.$$  \hspace{1cm} (6)

Kawabata calculated the residual C.E.S.R. linewidth $\delta \omega_0$ and shift of resonance $\delta \omega_0$ at low temperatures for $h/\tau \Delta \ll 1$ and $\delta \omega_0 / \Delta \ll 1$, and found

$$\delta \omega_0 / \omega_o \sim h / \tau \Delta; \quad \Delta \omega_0 / \omega_o \sim - h / \tau \Delta$$  \hspace{1cm} (7)

which according to eq. (6) vanishes for small $N$ or small $d$ and varies as $d^3$ in contrast to the result eq. (3) for larger particles. For pure metals with small spin orbit coupling and small $g$-shift one then expects the C.E.S.R. linewidth to be extremely small in the regime of small $\rho$

However, experiments [8] suggest that exchange interactions with paramagnetic impurities and magnetic hyperfine interactions may have pronounced effects on the observed resonances. We may assume that the effects of impurities within the volume of the small particles are negligible. However, impurity spins in the matrix (concentration $c_m$) adjacent to the particles, within a distance equal to the matrix lattice constant $a_0$ of the surface, will couple to the conduction electrons with a reduced average exchange constant $J$ [8]. The effective concentration of impurities with respect to the volume of the particle will be $c_m$, multiplied by the surface/volume ratio $= 6 c_m a_0 / d$. The C.E.S.R. linewidth from this interaction is

$$\delta \omega_0 / \omega_o = 2 S(S + 1) c_m J (a_0 / r_s) / 3 kTN^{1/2}.$$  \hspace{1cm} (8)

Even in pure metals with no matrix impurities at low temperatures, the hyperfine interaction remains, which produces an inhomogeneously broadened line [8] consisting of spin packets, each packet possessing an enhanced relaxation time no shorter than $1/\delta \omega_e$ of eq. (7). Thus we have

$$\delta \omega_e = (a / 2 \hbar) / N^{1/2},$$  \hspace{1cm} (9)

where $a$ is the s-electron hyperfine coupling constant.

3. The nuclear magnetic resonance. — The N.M.R. occurs at the frequency

$$\omega = \mu H / \hbar$$  \hspace{1cm} (10)

with $\mu$ and $I$ being the nuclear magnetic moment and spin, respectively. The resonance is shifted in metals by the electron-nuclear hyperfine interaction

$$K = \delta \omega / \omega = a \chi_n \Omega / \mu \mu_n \mu$$  \hspace{1cm} (11)

where $a$ is the s-electron hyperfine coupling constant in the metal and $\Omega$ is the atomic volume. The Pauli susceptibility, $\chi_p$, in the non-interacting electron approximation is

$$\chi_p (3/2) \mu / N / E_F = 2 \mu / \Delta.$$  \hspace{1cm} (12)

If, in the even particles the ground state of the electronic system is a singlet, the susceptibility indicated by eq. (12) for normal bulk material vanishes because of the pairing. For the odd particles, the ground state is appropriate to the single unpaired spin [3], and the temperature dependence of the susceptibility is

$$\chi / \chi_p = \Delta / 2 kT.$$  \hspace{1cm} (13)

For negligible spin-orbit coupling, the low temperature susceptibility for small even particles is $[3]$

$$\chi(T) / \chi_p = 3.8 kT / \Delta,$$  \hspace{1cm} (14)

in which the levels available for excitation are in proportion to the temperature. This applies to the orthogonal statistical ensemble.

In the case of intermediate spin-orbit coupling the symmetries are typical of the symplectic distribution, in which neighbour levels are probable as the fourth power of neighbour spacing, in which case $[3]$ the leading low temperature term is proportional to $T^4$,

$$\chi(T) / \chi_p = 2.02 \times 10^4 (kT / \Delta)^4,$$  \hspace{1cm} (15)
The numerical coefficients in eq. (16) are of order unity but the precise values remain to be determined. Shiba's result for $\chi(0)/\chi_0$ must be approximately correct on physical grounds and by analogy to the similar case of the superconductor [11], but his temperature dependence is probably incorrect owing to the fact that he considered only the case of equal level spacing, and used the grand canonical ensemble which does not conserve electron number and permits of excitations not allowed in the analyses of Kubo and Denton. On the other hand, although Denton et al. use more realistic energy level distributions and consequently arrive at better forms for the temperature variation of $\chi$, they omit consideration of the effects of the electron dynamics and the resulting residual susceptibility $\chi(0)$. Equation (16) should be useful as an approximate interpolation formula until a unified theoretical treatment of all of the important effects is available. The important N.M.R. line broadening arises from indirect coupling of the nuclear magnetic moments to impurity spins in the matrix via the RKKY spin density oscillations in the conduction electron system. The width may be estimated following the arguments in the development of eq. (8) for the C.E.S.R. impurity width, with the addition of the $K$ factor (from eq. (11)) accounting for the hyperfine interaction and, a factor arising from an average over the RKKY range function [13].

$$\delta \omega / \omega = c_m K I(a_0/d) / 3 kT.$$  

(17)

This broadening is inversely as the particle diameter, provided $c_m$ is large enough to provide an average of one or more impurity spins per particle.

The behaviour of superconducting small particles has been investigated [5, 15, 16], but will not be discussed here.
4. Experimental results. — 4.1 C.E.S.R. — In the following we refer to selected experimental results without attempting to be exhaustive. The first report [6] of a quantum size effect indicated by C.E.S.R. the presence of paramagnetism in the odd particles in a sample of lithium, and vanishing Pauli paramagnetism in the even particles. Later results have since been obtained on small particle samples of lithium [9d], and of aluminum [9b, 10a] above the superconducting transition temperature. In these cases, eqs. (7) and (14) are expected to hold, since the spin-orbit couplings are small. Certainly the condition \( \chi(0) = 0 \) seems to hold for even particles. The C.E.S.R. result for aluminum [9b] appears to be consistent with eq. (7) with appropriate size distributions and assuming g-shifts and line-widths of similar magnitudes.

Silver particles [9a] supported in a solid inert gas matrix show the expected odd particle paramagnetism and narrowed C.E.S.R. lines with position and width consistent with eq. (7). These are interpreted as arising from particles in the size distribution with diameters below 20 Å with an inferred \( \Delta g = +0.032 \) for bulk silver. Experiments at several frequencies confirm the \( \omega_c \) dependence in eq. (7). The linewidth of around 30 gauss is attributed to the sharp cutoff of the quantum size effect narrowing above 20 Å. A long easily saturated low-field tail appears to be associated with the smallest particle and may be hyperfine broadening, which according to eq. (9) is \( 400/N^{1/2} \) gauss for silver, in approximate agreement with experiment.

The experiments on sodium were performed in irradiated-annealed samples of NaN\(_3\) and showed no direct indication of Kawabata line narrowing [7, 8]. The size distribution of particles ranged from around 10 Å to 200 Å or more. The effects of size and temperature are related to the impurity and phonon broadening, the former corresponding [8] to eq. (8) with \( J_{cm} = 4 \times 10^{-8} \) eV in the 100 Å range. That no evidence was found for Kawabata line narrowing is perhaps not surprising in view of the role played by matrix impurities. A broad (30 gauss) line appeared as a background under the sharper signal at the same g-value and was easily saturated at low microwave powers at the lowest temperatures. This was attributed to the smallest particles not affected by impurities, with long relaxation times and inhomogeneous hyperfine broadening, according to eq. (9) which is equivalent to \( 175/N^{1/2} \) gauss for sodium. This is consistent with the observed width for particles containing around 100 atoms \( (d = 25 \text{ Å}) \).

The experiments on lithium particles in a solid rare gas matrix [9d] reveal narrow lines and long relaxation times in the particle size range of 10-15 Å. The linewidth is proportional to the applied field, with a residual width which is somewhat too small to be consistent with a hyperfine broadening. At this time it is difficult to construct a consistent picture for g-values and hyperfine contributions to the linewidths for the C.E.S.R. results in lithium, sodium, aluminum and silver.

4.2 N.M.R. — As we have already indicated, the metals lithium and aluminum provide results in agreement with the condition \( \chi(0) = 0 \) for even particles [6, 10]. For copper the existence of the low field tail on the line gives evidence for the onset of paramagnetism [10b] in the odd particles and for the result \( \chi(0) \neq 0 \) for even particles. For a narrow distribution of particle sizes [11] the result indicates more precisely that \( \chi(0) \) is a function of particle size as implied by the first term of eq (16), and the low temperature dependence appears to favor the orthogonal ensemble according to the second term of eq (16). It should be noted particularly that the value of \( \rho \) so indicated for \( d = 40 \text{ Å} \) corresponds to a spin relaxation time \( \tau = 5 \times 10^{-11} \text{ s}^{-1} \), which is equivalent to an average spin flip per two hundred surface encounters of the conduction electrons. This would correspond to a C.E.S.R. line considerably too broad to observe, and the N.M.R. results thus provide information on electron spin relaxation rates in a range which is inaccessible to direct C.E.S.R. measurements.

5. Conclusions. — The experimental evidence favours the expected quantum size effects as to: difference in behaviour of even and odd particles; reduction in Pauli susceptibility for even particles; Curie susceptibility for odd particles; role of spin-orbit coupling in both static and dynamic characteristics of the conduction electron spin system; complementary aspects of N.M.R. and C.E.S.R. in elucidating the electron spin relaxation rates; role of impurity broadening and RKKY spin density oscillations. The contributions of the hyperfine interactions are less clear. The interactions with paramagnetic impurities in the matrix are interesting problems, but they are also a hindrance in measuring and understanding the properties of isolated particles. With a better knowledge of the behaviour of the pure particles, one could hope to address the problem of interactions between particles and the embedding matrix, and the interesting question of leakage of the conduction electron wave functions out of the metal and into the matrix.

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