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LETTER TO THE EDITOR

Evidence from NMR for temperature-dependent Bardeen–Friedel oscillations in nanometre-sized silver particles

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Abstract. The abrupt discontinuity of the background in the semi-infinite jellium results in a decaying oscillatory (Bardeen) spatial response of the electron gas. Related phenomena are the Friedel oscillations around an impurity in a metal, and the Ruderman–Kittel coupling between two localized magnetic moments embedded in a sea of conduction electrons. We have found that the ^{109}Ag ($I = \frac{1}{2}$) NMR linewidth in nanometre-sized supported (and therefore isolated) silver particles shows a size effect that may be due to Bardeen–Friedel oscillations. The linewidth is also temperature dependent, in a way that cannot easily be explained as an effect of paramagnetic impurities; we suggest that thermal vibrations, known to have comparatively large amplitudes in small particles, wash out the abruptness in the background-charge discontinuity, and thus diminish the amplitude of the oscillations.

The first discussion of size effects in NMR of metals seems to be that of Charles and Harrison [1]. They ascribe an observed broadening of the NMR line in thin filaments of lead to surface-induced spatial variations in the density of Fermi-level electrons, and argue that the Knight shift at a distance x from the surface, $K(x)$, should vary as $\sin(2k_{\text{F}}x)/2k_{\text{F}}x$. A very similar phenomenon has been treated theoretically by Kautz and Schwartz [2], who calculated the position-dependent electron-spin susceptibility in a simple metal bounded by a surface. They too find Bardeen–Friedel [3, 4] oscillations, with the asymptotic $\sin(2k_{\text{F}}x)/2k_{\text{F}}x$ behaviour, but seem to have been unaware of the experiments on lead NMR.

Another line of research has been focused experimentally on NMR of copper particles [5, 6, 7, 8], and theoretically on the quantum size effect for the susceptibility predicted by Kubo [9], and treated in more mathematical detail by Denton, Mühlischlegel and Scalapino [10]. The corresponding NMR quantity is the temperature dependence of the average Knight shift (rather than the linewidth), given by the centre of gravity of the NMR absorption. In several cases, however, a temperature-dependent linewidth was found, and usually ascribed to extrinsic sources, such as (unidentified) magnetic impurities or (copper) oxides. There have been indications of a correlation between linewidth and particle size in other systems as well: in studies of superconductors [11, 12] it has been dubbed the ‘small-particle effect’.

While ^{207}Pb and ^{195}Pt have nuclear spin $\frac{1}{2}$ and hence NMR that is sensitive to magnetic couplings only, both ^{63}Cu and ^{65}Cu have spin $\frac{3}{2}$, which makes the spectra sensitive to the electric field gradient as well. In cases where the magnetic Charles–Harrison effect

is important, electric charge-density effects (nuclear quadrupole coupling) must also be important. Indeed it has been reported that the linewidths do not scale with field in a simple way [7, 8], indicating that there are both magnetic and electric (quadrupole interaction) effects. It is therefore possible that the NMR of copper nuclei in the surface region is completely wiped out.

King *et al* [13] have suggested that this is the case in their experiments on silica-supported copper catalysts, but Ido and Hoshino [6], working with unsupported and probably oxidized particles, think that there are magnetic effects in the surface layers. A further complicating feature of the observed copper lineshapes for small samples at low temperatures is that they show tails towards low field. This implies that the average Knight shift is not given by the frequency of the absorption maximum.

The metallic properties of silver are not qualitatively different from those of copper. For NMR however, both ^{107}Ag and ^{109}Ag have the advantage of being spin- $\frac{1}{2}$ nuclei (and the disadvantage of a low gyromagnetic ratio). In bulk silver, the FWHM linewidth ΔH is of the order of 0.75 G; in a 7 T field this gives $\Delta H/H = 11$ ppm, compared to a Knight shift of $K = 5200$ ppm. For copper, the corresponding figures are $\Delta H/H = 120$ ppm, $K = 2500$ ppm. It follows that, apart from sensitivity problems, silver is the better choice: magnetic effects are expected to be larger than in copper, and electric effects absent, unlike in copper. We have studied the ^{109}Ag NMR alumina-, titania- and silica-supported silver particles, prepared by several different wet-chemical methods. Their loadings were between 1 and 10 wt%. An average particle diameter d was determined from the broadening of the (111) line in x-ray diffraction. Values of d range from 13 to 80 nm. The particle size distributions are not well known: electron microscopy suffers from very poor contrast, and only rarely have we been able to obtain usable micrographs. There are indications that the large reactivity of silver easily leads to strongly asymmetrical or even bimodal size distributions [14]. Transition metal impurity levels were below our detection limit of 50 ppm of sample weight for each element. The NMR experiments were generally performed in 7 T or 8 T fields, and sample temperatures ranged from 15 K to 400 K. The spin-echo amplitude (the integral of the absorption lineshape) followed Curie's law, indicating that the same number of silver atoms were seen at all temperatures.

All NMR lines are symmetrical, and their centre is at the bulk metal resonance position. The spin-lattice relaxation time T_1 has the bulk value as well. The widths of the lines are dependent on field, temperature and size. The full lineshape (which is neither Lorentzian nor Gaussian) scales linearly with field when going from 4 T to 8 T; at fixed field the lineshapes observed at 80 K and at 20 K differ only by a scaling factor; the latter, however, is not 80/20 (as expected for a Curie law broadening mechanism) but approximately 1.6 (slightly sample dependent). It follows that the linewidth does not scale as field/temperature (see figure 1), as expected for paramagnetic-impurity broadening in the dilute limit. If we try to fit the temperature dependence of the linewidths to a Curie-Weiss law, the Weiss temperatures must be between 40 K and 100 K, which would require impurities at the metallic percentage level [15]. The ^{207}Pb linewidths observed by Charles and Harrison [1] (probably at room temperature) scaled with field, and were of the order of 550–1000 ppm (the average Knight shift K was that of the bulk, $K = 14\,700$ ppm). In terms of linewidth/ K this gives 0.04–0.07. For comparison, our 13 nm sample has, at room temperature, $\Delta H/H = 0.025$; but at 20 K it is more like 0.15.

At constant temperature, the linewidth decreases with increasing diameter d : it goes not slower than d^{-1} , and not faster than d^{-2} (see figure 2). In the Charles-Harrison model [1], the second moment of the line $\Delta\bar{\omega}^2$ is proportional to the inverse of a typical particle dimension. It is not certain, however, that the square root of this quantity is a useful

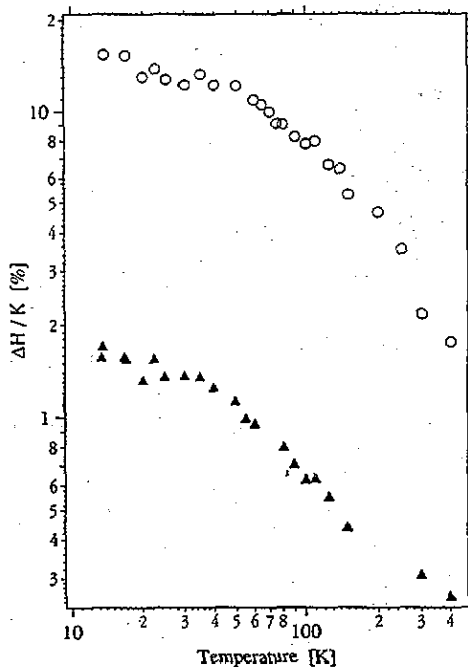


Figure 1. Linewidths ΔH (full widths at half maximum, FWHM) of ^{109}Ag NMR in two samples, as a function of temperature. The unit of linewidth is the bulk Knight shift K (5.215×10^{-3} relative to the Ag^+ ion at infinite dilution in H_2O at 300 K, decreasing slightly towards lower temperature). The typical particle diameter d as determined by broadening of x-ray profiles is: ○, $d = 13$ nm; ▲, $d = 80$ nm.

measure of the linewidth: using their model to calculate the fourth moment $\Delta\bar{\omega}^4$, one finds that $\Delta\bar{\omega}^4/(\Delta\bar{\omega}^2)^2$ increases as d . Therefore the moments of the line are mainly determined by the wings of the signal, and the FWHM linewidth is expected to vary faster than $d^{-1/2}$. A rough estimate may be obtained as follows. The calculation by Kautz and Schwartz [2] indicates that for silver (electron density parameter $r_s \simeq 3$) the relative shift of the NMR frequency of surface atoms (with respect to the bulk) might be as large as ± 0.15 (of the order of $\Delta H/K$ for our smallest sample at low temperatures). In the 7 T field, this amounts to 70 times the FWHM linewidth of the bulk; we put the observed linewidth proportional to the fraction of nuclei that have their resonances shifted outside the bulk linewidth. Using the asymptotic relation

$$K(x) \propto (2k_{\text{FX}})^{-1}$$

these nuclei are found to be in the ten atomic layers (2.84 nm) closest to the surface. In the largest-sized sample, the fraction of atoms in this region is about one tenth; in the smallest sample it is five times larger. The observed linewidth ratio is ten, in sufficient agreement with this rough estimate. From this estimate we expect the linewidth to decrease as d^{-1} for diameters large compared with 5.7 nm.

In the studies of copper NMR, it has been proposed that the observed temperature-dependent magnetic broadening might be due to copper oxides [6, 7]. We have chemisorbed

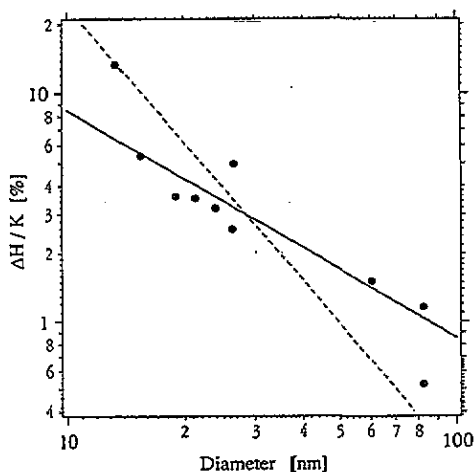


Figure 2. Linewidths $\Delta H/K$ (units as in figure 1) as a function of the typical particle diameter d , determined from broadening of x-ray profiles. The lines have slopes d^{-1} and d^{-2} . We suggest that for large-sized samples, with comparable size-distribution functions, the experimental points should follow a d^{-1} relation, and that the scatter is due to 'unlike' size distributions.

a monolayer of oxygen at 450 K on the 20 nm sample, and found no observable change in the NMR behaviour. A similar observation has been made for copper [13], using N_2O adsorption and reaction. In the ^{109}Ag NMR study of supported catalysts by Plischke *et al* [14], a resonance has been found only when particles larger than roughly 50 nm are present in the sample. Oxygen adsorption broadened the lines in highly loaded Fe-doped Ag/SiO_2 catalysts, but did not affect the linewidth in undoped $\text{Ag}/\text{Al}_2\text{O}_3$ with loadings comparable to those we applied. At room temperature, all linewidths were comparable to those of the bulk. A determination of T_1 at 173 K is reported, but the linewidth at that temperature has not been stated.

The phenomenon of size- and temperature-dependent magnetic broadening of NMR lines in noble metals, and perhaps also lead and tin [11, 12], but not in d-band metals like Pt [16, 17], therefore might well arise from intrinsic properties of small particles; certainly extrinsic sources of broadening have never been clearly identified. The theoretical problem is that, while the Charles-Harrison-Kautz-Schwartz mechanism can at least qualitatively account for the size dependence, no alternative (with respect to the impurity hypothesis) explanation for the temperature variation seems to be available. For particles of the size used in our work, we do not expect electronic-shell effects to be important [18].

Our experiments on nanometre-sized silver particles show a NMR line broadening that is:

- magnetic in origin;
 - symmetric about the bulk silver resonance position;
 - size dependent;
 - unlikely to be due to paramagnetic impurities but nevertheless temperature dependent;
- and
- at low temperatures visible in particles as large as 80 nm.

The symmetric lineshape strongly suggests:

- a broadening mechanism that changes sign with distance (or orientation) from the source;
- a size dependence of the source on the surface;
- a temperature dependence that is sensitive to thermal motion;
- the observation in rather large particles that the range is fairly large in terms of the lattice constant.

The first two characteristics are those of the Charles–Harrison–Kautz–Schwartz mechanism, where the decay is inversely proportional to distance, with a characteristic length $(2k_F)^{-1}$ (0.04 nm for silver) and where the only possible temperature dependence is through Fermi surface blurring, which is a very small effect.

Concerning the decay length, it is interesting to note that the relation between composition and transition temperature of metallic spin glasses indicates an interaction range larger than expected from a (mean-free-path-corrected) Ruderman–Kittel–Kasuya–Yoshida interaction [15]. This suggests that a more quantitative treatment of the linewidth/size relationship than that given above might require a form different from

$$K(x) \propto \frac{\sin(2k_F x)}{(2k_F x)}$$

The decrease of the linewidth with increasing temperature is not accompanied by measurable effects in the nuclear spin–lattice relaxation, as usually found in the case of ‘motional narrowing’ where each nucleus rapidly samples a variety of environments [19]. We are probably seeing here a magnetic and surface equivalent of the Bayer mechanism [20] for the averaging out of NQR frequencies through phonon-like motion. The mechanism in the present case would be a blurring, with increasing thermal vibrations, of the abruptness of the jellium background-charge cut-off leading to a more gradual transition, and an associated diminishing of the amplitude of the Bardeen–Friedel oscillations. Such an effect might be especially important in small metallic particles, where increased vibration amplitudes are seen in the Debye–Waller factor [21] and in a lowering of the melting temperature [22].

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