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The NMR of small (sub 50 Å) copper particles at low temperatures (to 1.5 K) and high magnetic field (13 T)

David P Tunstall†, Peter P Edwards‡, Jamie Todd†¶ and Melvyn J Williams§

† Physics and Astronomy Department, University of St Andrews, St Andrews, Fife KY16 9SS, UK

‡ School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

§ Department of Chemistry, University of Cambridge, UK

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Abstract. As part of a programme to investigate the size-dependent electronic structure of small solids, we have recently reported low-temperature data (1.5–4.2 K) on the ^{63}Cu nuclear magnetic resonance (NMR), at high magnetic fields, in a range of tiny particles of copper metal, prepared by a colloidal route, paying particular attention to the changes in the peak Knight shift with particle size. In the present work we have extended the interpretation of these peak shifts and include new direct measurements of both the linewidths and the nuclear spin–spin relaxation time T_2 of the copper nuclei in these small metallic particles. The linewidths observed are very large, typically in the range 100–700 kHz, and we indicate that they may have a magnetic origin, intimately connected with the particle size distribution. The T_2 values measured become very large as the particle size diminishes. The linewidths and T_2 values appear to be correlated.

1. Introduction

The geometric and electronic properties of small metal particles continue to attract interest; there are connections to the metal–non-metal transition, catalysis, inorganic clusters, zero-dimensional superconductivity, and more recently the quantum dots and narrow quantum wells of modern semiconductor structures (Kobayashi 1990, Kimura 1990, Persans *et al* 1992, Slichter 1986). The magnetic properties at low temperature depend critically on whether the particle contains an odd or an even number of electrons.

Halperin (1986) provides an excellent review of the quantum size effect on small metal particles, particularly of the theoretical aspects; for the reader's convenience we mention here some of the salient features of this review. Starting from a careful consideration of the behaviour of the spacing δ of electronic energy levels as one moves from bulk metal to a small metal particle of volume V, $\delta \sim V^{-1}$, Halperin goes on to consider the Kubo analysis (Kubo 1962), based on the assumption of equal energy level spacing. This assumption however leads to an inconsistency at small level spacings, and therefore the review moves on to consider the more realistic electronic energy level distribution based on random matrix theory, the approach of Denton and co-workers (1973). In this approach the symmetry of the Hamiltonian of the system controls the behaviour of the system, through the energy level distribution. The Poisson, symplectic, orthogonal and unitary distributions correspond to particular experimental and sample conditions. The magnetic field dependence of the even-particle susceptibility is shown to be a direct measure of a function describing the

¶ Now at Department of Chemistry, University of British Columbia, Vancouver, BC, Canada.

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correlation between electronic energy levels, the two-level correlation function $R(x)$, where x is proportional to the separation in energy of the two levels concerned. Finally, Halperin (1986) addresses the problem of the presence of spin–orbit interaction, reviewing the theory of Sone (1977) amongst others. As with the problem of the non-disappearance of the spin susceptibility in superconductors on cooling to low temperature in the presence of significant spin–orbit interaction, so the mixing of spins and orbital functions leads, in the small-particle problem, to reductions in the effect of size on both even- and odd-particle susceptibility.

Nuclear magnetic resonance has proved to be a particularly useful, and microscopic, probe of the reduced dimensionality effects characteristic of small metal particles (Yee 1973, Kobayashi and Katsumoto 1987). The main attributes of this non-intrusive technique are its easy differentiation of the intrinsic signal from the small metal particles (which typically exist in the sample as a minority of material, being supported on an appropriate substrate), and its inherent sensitivity to the magnetic susceptibility and electronic structure of the small particle. It is important to note that in this context the electronic magnetic susceptibility is *the* critical property that differentiates most sharply the electronic structure of the bulk from that of the small particle in metal particles; the idea that a metal particle with 1000 electrons could have dramatically different magnetic properties from a particle with 1001 electrons provides a compelling motivation to study the magnetic susceptibility and the NMR in such systems. In previous studies of the NMR of small metal particles (Yee 1973, Kobayashi and Katsumoto 1987), the Knight shift and spin–lattice relaxation time have been the principal targets of interest; relatively little attention has been paid to the nuclear spin–spin relaxation time T_2 and the NMR linewidth.

The vast majority of previous investigations in this field has utilized sample preparation methods based on high-temperature evaporation in vacuum of the metal onto a suitable substrate. The present study, however, is on colloidal copper particles, prepared by a variety of synthetic routes, involving the solution-based reduction of copper salts at ambient temperature, followed by loading onto a suitable, high-purity, substrate. There are several notable advantages in the use of colloidal metal routes for the fabrication of small metal particles (Kirkland *et al* 1990); these include the control of the particle size distribution within the sample, the absence of paramagnetic centres on the chosen substrate, and the ability to change the amount of metal (loading) available within the sample. We have found that all three can be judiciously optimized by careful synthetic routes and preparative operations, involving the colloidal metals copper, silver, gold, platinum and palladium (Kirkland *et al* 1990).

The focus of this present contribution to the literature on the NMR of small metal particles is to discuss further the interpretation of the peak shifts, taken at very high magnetic field, in these samples fabricated by this relatively new procedure and to present new data on the linewidths and T_2 values that we have measured.

The organization of this paper is as follows. In the following section we present our results on the characterization of our colloidal samples and in the next section we describe the NMR results. Some relevant theory is then summarized, followed by a discussion, with particular focus on lineshape analysis and the behaviour of T_2 in our systems.

2. Synthesis and characterization

The colloidal copper particles have been exclusively synthesized by the reduction of copper(II) acetate in alcohol by either hydrazine hydrate or sodium borohydride (Curtis *et al* 1988a, 1988b, Williams 1991). The resulting particles have then been deposited onto

a support (usually Aerosil silica) for further experimentation. Some of the procedures have been developed by Curtis *et al* (1988a). Full details of the various synthetic routes taken to obtain samples with different mean particle sizes have been described by Curtis *et al* (1988a, 1998b) and Williams (1991).

All samples were examined by electron microscopy, primarily to check on the degree of dispersion, and on the size of the samples (Kirkland *et al* 1990, 1991). We characterize each sample by its mean volume weighted particle diameter $\langle d \rangle_w$ (Kirkland *et al* 1990). Optical spectroscopy, using a Pye Unicam spectrophotometer, was an invaluable aid during the synthesis procedures. We have already shown (Kirkland *et al* 1990, Curtis *et al* 1988a, b, Kirkland *et al* 1991, Curtis 1989, Williams 1990) the full details of these aspects of the characterization. For ease of reference we reproduce in figure 1 a typical histogram of one of our samples.

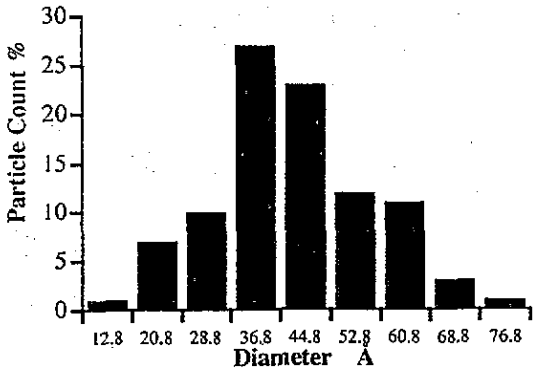

Figure 1. A histogram for the $\langle d \rangle_w = 44$ Å sample.

We attempted also to characterize the mean particle size from the broadening effect of small particles on x-ray diffraction lines (Williams 1991, Kirkland *et al* 1993). The procedure consistently gave particle sizes smaller than those obtained by direct observation by electron microscopy (Matyi *et al* 1987).

Electron spin resonance (ESR) at 5 K of copper particles of mean diameter $\langle d \rangle_w = 60$ Å, 80 Å and 120 Å, prepared by similar routes, produced evidence for a very small signal from the silica support in the samples but, importantly, no evidence of any signal from the copper particles themselves. Perhaps the latter observation correlates with a literature search (see for example the section on ESR in the noble metals in the article by Halperin (1986), where apparently there has not been any ESR work on small metal particles of copper). It also correlates with the transmission electron spin resonance (TESR) work (Schultz and Latham 1965) on copper where the low-temperature (1–20 K) linewidth of 38 μm copper foil is very large. This TESR work concludes that surface scattering is strong in copper. In the review (Halperin 1986) it is made clear that many of the ESR measurements that have been made in small metal particles are by no means easy to make or easy to interpret.

One further useful ESR characterization that we undertook was to deliberately allow the 60 Å particles to become oxidized (Williams 1991); the sample instantly turned blue and a broad, but very strong, ESR signal emerged with a g-value of 2.095, nearly isotropic. In contrast, in the sample with $\langle d \rangle_w = 120$ Å, the particles became dark green on oxidation, and produced a much weaker and broader ESR signal, clearly anisotropic in character.

To summarize the ESR results, the sample colour and oxidation are strongly correlated, giving us confidence that our NMR samples were not oxidized; no conduction ESR could be observed, and paramagnetic impurities appear to be almost totally absent, even in the substrate.

3. NMR results

The data were all taken with a spin echo (Hahn 1950) sequence, with point-to-point sweeping of the magnetic field to accumulate the spectra. In figure 2 we show a 1.5 K spectrum from the sample having $\langle d \rangle_w$ = 34 Å. The resonant fields corresponding to bulk copper metal and $3d^{10}$ Cu^+ resonances at this frequency have been marked on the field axis. We draw attention to the huge linewidth, ~700 kHz, of the small-particle resonance, with substantial intensity both to larger shifts than copper metal (to the left of the metal marker), and to negative Knight shifts (to the right of the bare copper marker). Note also that the peak value of the Knight shift is reduced well below the value for copper metal.

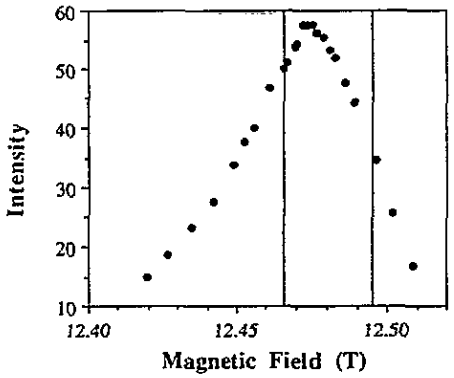

Figure 2. The ^{63}Cu spin echo intensity for the $\langle d \rangle_w$ = 34 Å sample, plotted as a function of the applied magnetic field, at 1.5 K. The markers at 12.466 T and at 12.494 T refer to the positions of the bulk copper resonance and the bare copper resonance, respectively.

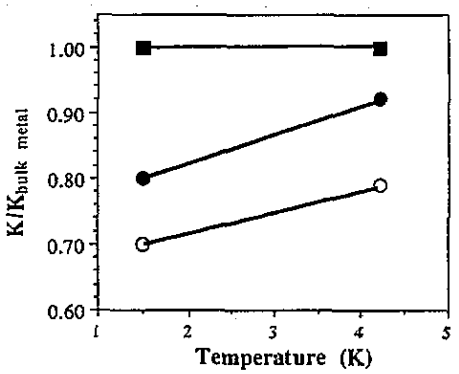

Figure 3. The Knight shift, K, as measured at the peak of the swept-field spectrum, as a function of temperature for three of the samples. The shift is expressed as a fraction $K/K_{\text{bulk metal}}$ of the bulk metal shift. The lines are guides to the eye. Open circles, $\langle d \rangle_w$ = 34 Å; filled circles, $\langle d \rangle_w$ = 44 Å; filled squares, $\langle d \rangle_w$ = 80 Å. Error bars on this data are approximately ±5% in $K/K_{\text{bulk metal}}$.

In figure 3, our peak Knight shift data at 141 MHz for three samples at two temperatures (2.5 K and 4.2 K) are reproduced (figure 10 from [1]).

In addition, we measured the linewidth of a 120 Å particle sample at both 30 MHz and at 141 MHz, revealing a 100 kHz linewidth at 30 MHz, in comparison to the 220 kHz recorded on the same sample at the higher frequency. This appears to be consistent with a linear variation of linewidth with applied magnetic field, since the spin echo technique that we employ has an in-built instrumental broadening effect of about 60 kHz. (This intrinsic instrumental broadening was measured on a sample of large particle size, what one would term bulk copper (and therefore with an intrinsically narrow line), in an inhomogeneous field such that an echo could be observed, with the spectra assembled by the same swept-field technique as employed for the small-particle measurements above. We first destroyed

the free induction decay by placing the sample in an inhomogeneous field such that the inhomogeneity over the sample was about 20 kHz, and then assembled a point-by-point spectrum using the same parameters as were previously used in acquiring the spectra for the small-particle samples. Under our experimental conditions the measured linewidth was about 60 kHz.)

We have also measured the NMR linewidths and T_2 values at 141 MHz in a series of different samples, with different particle sizes, $\langle d \rangle_w$ = 34 Å, 44 Å, 80 Å and 122 Å. In figure 4 we show the variation of T_2 (measured by a 90–τ–180 pulse sequence (Hahn 1950), with variable τ, at the fields corresponding to the maximum echo) and total, swept-field, spectrum width (taken at half height) as a function of particle size. All these data were taken at 141 MHz and a temperature of 1.5 K. The same data at 4.2 K show almost no change, within experimental error. Striking features of figure 4 are, at small particle size, the enormous linewidths, apparently linked to a large increase of T_2.

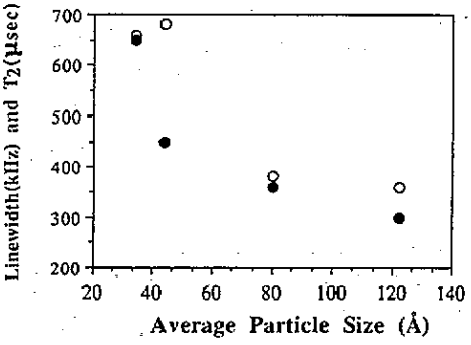

Figure 4. Linewidth at half height, and T_2, plotted against particle size at 1.5 K. Open circles, T_2; filled circles, linewidth (full width at half maximum). The error on this data is approximately ±5% on both ordinate parameters.

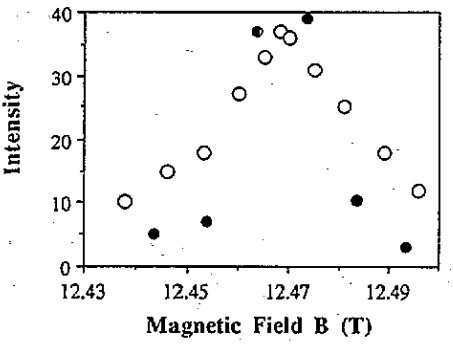

Figure 5. The model of the spectrum for the $\langle d \rangle_w$ = 44 Å sample at 4.2 K. Both experiment and theory are plotted; the theoretical spectrum at its peak has been normalized to the peak height of the experimental spectrum. Open circles, experiment; filled circles, theory. Details of the calculation are contained in the text.

4. Theory

We will briefly summarize some relevant theoretical considerations, with particular reference to the experimental conditions pertaining to our present experiments.

The experimental conditions are the following:

(i) temperatures between 1.5 K and 4.2 K,
(ii) high magnetic fields, usually ~12.5 T,
(iii) samples composed of particles of sizes between 34 Å and 122 Å.

These experimental conditions mean that the following energy scales are appropriate:

(i) refers to a range of thermal energies (kT) from 0.13 meV to 0.37 meV,
(ii) refers to a $g\beta B$-value of 1.45 meV, for an electronic g-value of two,

whilst

(iii) refers to a range of δ-values, where δ is the electron energy level splitting due to the size effect, of 0.13–6.1 meV.

All these energy scales are comparable, so the relevant symmetry that governs the experimental conditions needs to be considered carefully, and individually, for each experiment. Existing theories, reviewed by Halperin (1986) and Kobayashi (1990), are usually appropriate for the limiting cases $\delta \gg kT$, $g\beta B \ll \delta$ etc. However, these inequalities are rarely fully satisfied in our experimental conditions.

In our discussion section 5, we intend to use the following theoretical framework for the interpretation of our data. The electron spin susceptibility for even-numbered particles is given by (Sone 1977)

$$\chi_{\text{even}} = \{7.63\beta^2/\delta\}\{kT/\delta\}\{1-\rho\}^2 + \{2\beta^2/\delta\}\{2\rho - \rho^2\} \tag{1}$$

where ρ is a spin–orbit coupling parameter. This equation will be used as the basis of our discussion of the peak positions as a function of both temperature and particle size; it reflects the tendency for spin–orbit coupling to wash out quantum size effects. For example, for $\rho = 1$, strong spin–orbit coupling, the first term in equation (1) is zero and the second term reduces to a standard Pauli term.

5. Discussion

We have presented data, taken mainly in very high magnetic field, on the enormous linewidths, the much smaller peak shifts and their temperature dependences, and on the correlation between linewidths and T_2. We have also described an experiment on a sample with largish particles ($\langle d \rangle_w \sim 120$ Å) that suggests that the origin of our linewidths may be magnetic, rather than quadrupolar.

Previous theoretical and experimental studies in this area have generally encountered small linewidths, or have ignored the linewidth and concentrated on explaining the shifts, usually defined by the peak shift. Another prominent feature of previous theoretical studies have been the universal belief that the experiments relate to particles with even numbers of electrons. None of these previous studies has addressed the problem of the T_2 values.

We discuss first the NMR peak shift, figure 3, which we interpret directly via equation (1). (Bear in mind that the enormous widths cast some doubt on the validity of any analysis based on peak shifts. For example a calculation of the first moment of the spectrum of figure 1 indicates that the mean NMR intensity lies at a shift value (from the metal line) of about a half of the peak shift. We will address this problem again later.) The implicit assumption here is that we are observing only even-numbered particles. There are many precedents for such an assumption in earlier work (Halperin 1986), although in discussing the linewidths shortly we cast some doubt on the validity of this assumption. We have already featured the experiment–theory agreement in the article of Williams *et al* (1991), where, from the $K(0)$ intercepts at $T = 0$ K in figure 3, we demonstrated a considerable disparity between the coefficients ρ needed to make equation (1) agree with experiment and the coefficients ρ deduced from separate measurements of electronic g-shifts.

The additional feature that we would like to discuss here is the possibility that this mismatch could be at least partially resolved via the quenching effect of the large magnetic field (the field was assumed to be small in the derivation (Sone 1977) leading up to equation (1)).

In the article of Williams *et al* (1991) we showed, in table 4, the following ratios for ρ^{OBS}/ρ^{CAL}: for the 34 Å sample, eight, and for the 44 Å sample, 4.6, where ρ^{OBS} is the value deduced from the Knight shift and where ρ^{CAL} is the value deduced from g-shift analysis. If we estimate the effects of field quenching from the $R(x)$ of the article by Halperin (1986), then values of 0.2–0.3 for $R(x)$ can be read off figure 5 of Halperin (1986) for our experimental conditions; we estimate this would lead, by reduction of ρ^{OBS}, to ratios of $\rho^{OBS}/\rho^{CAL} \sim 1$. We point out here that another important feature of figure 3 can also produce a value of ρ: the slopes of the lines should be governed by the first term in equation (1). A straightforward analysis yields values of $\rho = 0.18$ ($\langle d \rangle_w = 34$ Å particles) and $\rho = 0.42$ ($\langle d \rangle_w$ Å particles). It is interesting that these values are both less than the two initial values (before correction for the field-quenching effect) that emerge from the extrapolation of the Knight shift as T tends to 0 K. (Of course, using two points to define a straight line (figure 3) is stretching the data to their limits; we only seek to demonstrate a possibility here.) These two values will also be reduced once field-quenching effects are taken into account, just as they were in the discussion above. There is a clear need for more data in this area. Our conclusion, then, is that the zero-temperature extrapolation of the Knight shifts and the slope of figure 3 produce values of ρ roughly consistent with each other and with values of ρ that emerge from g-value shifts (Williams 1991).

Our second topic of discussion concerns the T_2 measurements. There is a marked enhancement of T_2 with decreasing particle size (figure 4). A small elongation of T_2 due to the rapid development of inhomogeneity in the spectrum can be understood, e.g. the quenching of the B-term (Abragam 1961) in the dipole–dipole interaction would be caused by inhomogeneity and would elongate T_2 by a factor of, at most, two. We seem to be faced here with a much larger effect, a multiplication, due to the inhomogeneity, from 150 μs to close to 700 μs, and there is, as illustrated in figure 4, a strong correlation between the inhomogeneous broadening, large T_2, and particle size.

A microscopic model such that T_2 tends to infinity would require that each copper nucleus was so shifted in resonance frequency from that of its near-neighbour copper nuclei that the pulses of the spin echo sequence flip only the central nucleus and not its neighbours. (The B_1 fields used in this study were typically 2.5 mT.) This model places the inhomogeneity observed in the linewidths on a nearest-neighbour scale, and any underpinning physics is difficult to visualize. An amorphous structure for the copper, with a different quadrupole interaction at adjacent sites, might just be appropriate here, but the apparently magnetic linewidth, at least in the sample with $\langle d \rangle_w \sim 120$ Å, would then pose a problem, as would the crystalline character of the x-ray spectra.

We may also speculate that, in the sample with small particles, the dipolar interaction is sufficiently long range that the truncation of dipolar sums induced by the presence of the particle surface may be enough to reduce the average dipolar broadening, and hence contribute to an elongation of T_2.

The question of the origin of the huge linewidths observed in the small-particle samples has not so far been addressed. The obvious possibility is that these widths are related to the spread of particle sizes present in any one sample (figure 1). Furthermore we have some evidence that both even and odd particles contribute to these widths. The experiments at 30 MHz and 141 MHz on this sample had already indicated that the broadening, at least in this 120 Å sample, increased with magnetic field, and was therefore of magnetic origin, rather than of quadrupolar origin (which would decrease with increasing magnetic field) (Abragam 1961). We assume, therefore, that the dominant broadening mechanism in the sample with $\langle d \rangle_w = 44$ Å is also magnetic in origin and correlated with the particle size distribution. This means that (i) different parts of the spectrum emanate from metal particles

of different sizes, and that (ii) the even-numbered particles contribute predominantly to the high-field side (and the odd-numbered the low) of the NMR spectrum.

We have constructed a simple model in an attempt to verify these ideas. We rely heavily on the assumption that the Knight shift K provides a direct measure of the electron spin susceptibility χ_s. These two parameters are assumed proportional to each other, with a proportionality constant B_{hf}, the hyperfine field. This is equivalent to the statement that within the unit cell the electron wave-function is not dependent on particle size or other experimental conditions. From well known bulk values of K and χ_s in copper (Cater *et al* 1977) we therefore know B_{hf}.

We have attempted this semi-quantitative fit to the spectrum of the sample with $\langle d \rangle_w$ = 44 Å at a temperature of 4.2 K. (For the purposes of this line profile calculation, we assume $\rho = 0$, i.e. no spin–orbit interaction. We assume equal numbers of even and odd particles, calculate their spectra separately, and then add the two to produce a composite spectrum.)

For the odd-numbered particles, we simply distribute one Bohr magnetron over the entire particle, and deduce what NMR shift this magnetization corresponds to, via our knowledge of B_{hf} (as outlined earlier we assume here that B_{hf} is independent of particle size). From the experimental histogram of particle sizes (figure 1) in a sample we can therefore deduce a theoretical NMR spectrum. (Clearly the possibility also exists of 3, 5, 7, ... Bohr magnetons on an odd-numbered particle, for the larger end of the range of particle sizes spanned by the histogram of sizes; however, this will provide only a small correction to our data for our small sample of $\langle d \rangle_w$ = 44 Å, which we have therefore ignored in this first-order calculation.)

For the even particles, we must build into the theory the $x = \{g\beta B/\delta\}$ dependence (Halperin 1986) of the electron susceptibility, i.e. the field-quenching effects discussed earlier. x has a value for the average-sized particle of the sample with $\langle d \rangle_w$ equal to 44 Å of about 0.5 in our experiments at high field. This is too big to ignore. We build this dependence in via the two-level correlation function $R(x)$ (see figure 5 of Halperin (1986)). Because the response to a magnetic field is in this case non-linear, and the Knight shift is proportional to the electron spin magnetization in the sample, we integrate the even-particle susceptibility with respect to field up to the value in our experiment. We have approximated this procedure for simplicity; we take the first term of equation (2.34) of Halperin (1986)

$$\chi = \{2\beta^2/\delta\} R(x)$$

and integrate from zero to $x = g\beta B/\delta$, for each bar (and therefore each δ) in our histogram of particle sizes in the $\langle d \rangle_w$ = 44 Å sample (figure 1). We can then deduce a Knight shift for each particle size within our distribution, and from that a theoretical, even-numbered particle, NMR spectrum can be synthesized.

Finally the spectrum from the even-numbered particles can be added to the spectrum from the odd-numbered particles to give a total NMR spectrum. The analysis is based on the orthogonal ensemble (Denton *et al* 1971), and is shown in figure 5 with, for comparison, the experimental lineshape.

The calculation is simplistic, but the agreement sufficiently encouraging to suggest that we have identified, and quantified, a significant source of broadening in the NMR spectrum. We recognize that this is in conflict with earlier analyses of the shift of the peak position, where it was assumed that the entire observed NMR spectrum originated from particles with even numbers of electrons. Until a more complete set of theoretical simulations of the spectra as a function of both particle size and temperature is calculated, one cannot be definitive in concluding that odd particles contribute to the spectrum. At the moment the

question is open; the agreement in figure 5 at least raises the possibility that odd-numbered particles may contribute to the overall spectrum.

However, the model of the linewidth, developed above and shown in figure 5, supposes that within each particle there is a uniquely determined Knight shift, and that the resonance of a single particle, if it could be observed, would look exactly like the resonance of an equivalent amount of bulk copper, but shifted because of the different Knight shift induced by the small size of the particle. There seems to be no room within this model for any elongation of T_2; the T_2 would be dictated by the T_2 mechanisms in each particle, and these would be identical to those present in bulk copper metal, i.e. 150 μs would be the expected value of T_2.

6. Conclusion

We have measured the spin echo ^{63}Cu NMR resonance as a function of magnetic field in a series of small-particle copper samples, prepared by a colloidal route, at predominantly high magnetic field and at helium temperatures.

We have interpreted the peak shifts monitored as a function of temperature and particle size, on an 'even-particle'-only model. The experimental evidence is that the spin–orbit effects are of the same order as would be predicted from a g-shift analysis of conduction ESR in copper.

We have measured linewidths and T_2 in several samples, and find a strong correlation between these two parameters. We speculate that an amorphous structure for the contributing copper sites might account for the unusual elongation of T_2. The crystalline character of the x-ray spectra of the particles counts against this explanation, however.

Finally we have advanced an idea connecting the linewidths with the histograms of particle sizes; whilst going some way to explain the large observed linewidths, and the presence of significant spectral intensity shifted to even lower applied field than the metal line, this model appears to conflict with the trends in T_2. Thus an integrated approach to the interpretation of NMR results in these small copper particles leaves us with several imponderables and conflicts; there is clearly a need for more experimentation, and this article should be regarded as only an interim report.

Acknowledgments

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References

Abragam A 1961 *The Principles of Nuclear Magnetism* (Oxford: Oxford University Press)

Curtis A C 1989 *PhD Thesis* Cambridge University

Carter G C, Bennett L H and Kahan D J 1977 *Metallic Shifts in NMR (Progress in Materials Science 20)* (New York: Pergamon)

Curtis A C, Duff D G, Edwards P P, Jefferson D A, Johnson B F G, Kirkland A I and Wallace A S 1988a *Angew. Chem. Int. Edn. (English)* **27** 1530

—— 1988b *J. Phys. Chem.* **92** 2270

Denton R, Muhlschlegel B and Scalapino D 1971 *Phys. Rev. Lett.* **26** 707

Hahn E L 1950 *Phys. Rev.* **80** 580

Halperin W P 1986 *Rev. Mod. Phys.* **58** 533
Kimura K 1990 *Phase Transitions* vol 24–26 (London: Gordon and Breach) p 493
Kirkland A I, Edwards P P, Jefferson D A and Duff D G 1990 *Annual Reports of the Progress of Chemistry* (Cambridge: Royal Society of Chemistry) p 247
Kirkland A I, Jefferson D A, Duff D G, Edwards P P, Gameson I, Johnson and Smith D I 1993 *Proc. R. Soc.* A **440** 589
Kirkland A I, Jefferson D A, Tany D and Edwards P P 1991 *Proc. R. Soc.* A **434** 279
Kobayashi S 1990 *Phase Transitions* vol 24–26 (London: Gordon and Breach) p 463
Kobayashi S and Katsumoto S J 1987 *J. Phys. Soc. Japan* **56** 2256
Kubo 1962 *J. Phys. Soc. Japan* **17** 975
Matyi R J, Schwartz L H and Butt J B 1987 *Catal. Rev. Sci. Eng.* **29** 41
Persans P D, Bradley J S, Chianelli R R and Schmid G (ed) 1992 *Mater. Res. Soc. Symp. Proc.* vol 272 (Pittsburgh, PA: Materials Research Society)
Schultz S and Latham C 1965 *Phys. Rev. Lett.* **15** 148
Slichter C P 1986 *Ann. Rev. Phys. Chem.* **37** 25
Sone J 1977 *J. Phys. Soc. Japan* **42** 1457
Williams M J 1991 *Thesis* University of Cambridge
Williams M J, Edwards P P and Tunstall D P 1991 *Faraday Discussion 92 Royal Society of Chemistry*
Yee P W 1973 *Thesis* University of California, Berkeley