# Influence of frequency and temperature on the conduction-electron spin-resonance linewidth and g value in copper

A. Stesmans and J. van Meijel
*Departement Natuurkunde, Katholieke Universiteit Leuven, Leuven, Belgium*

S. P. Braim
*Department of Physics, University of Exeter, Exeter, England*
(Received 5 December 1978)

The CESR linewidth and $g$ value of pure Cu is measured over the temperature range 4.2 to 50 K at the frequencies of 9.27, 21, and 59.6 GHz. The linewidth is shown to have a linearly frequency dependent, but temperature-independent term giving $0.040 \pm 0.002$ mT/GHz. A second term, when ascribed to partial breakdown of motional narrowing, is found to be much weaker than proposed elsewhere. The $g$ value is found also to be temperature and frequency dependent.

## I. INTRODUCTION

The first anomalous results of the influence of the observational frequency on the conduction-electron spin-resonance (CESR) linewidth and $g$ value of metals were reported by Lubzens *et al.*[1] in aluminum, mentioning[2] similar effects in copper and silver, although the $g$ value of the latter metals was found to be frequency independent. These results were obtained at 9.2 and 35 GHz using the transmission CESR technique (TESR). They interpreted their results using the many-body interaction theory of Fredkin and Freedman[3] (FF). This appeared to be satisfactory though later work did not support this conclusion.[4,5] In a subsequent paper[6] the frequency dependence of the residual linewidth $\Delta B_{res}$ of aluminum and copper was investigated at three frequencies (1.27, 9.2, and 35 GHz). It was proposed that $\Delta B_{res}$ for aluminum was linearly dependent upon the frequency $f$ while the same parameter for copper was proposed to be proportional to $f^2$. These results were also in contradiction with the FF theory for Al while the proposed $f^2$ dependence for copper suggested that the partial breakdown of motional narrowing theory[7] (BMN) could be applicable. More recent experiments carried out at higher frequencies[8] and a general reinterpretation of the aluminum results[9] showed that $\Delta B$ of aluminum contains a term $\alpha f$ ($\alpha$ is a constant independent of the temperature $T$) which was not recognized during earlier interpretations. In view of these results the linewidth and $g$ value of copper have been carefully investigated as a function of $f$, where the $f$ range has now been extended to 60 GHz. The $f$ dependence of $\Delta B$ in the phonon-dominated regime ($T \gtrsim 25$ K) is of much interest as the experimental data previously available in this region are poor.[2]

## II. EXPERIMENT

### A. Sample preparation

Samples were prepared by rolling out small pieces cut from polycrystalline Cu rods. The starting material[10] was either 99.999% or 99.9996% nominally pure Cu. During rolling, frequent etching and cleaning in either acetone, propanol, or distilled water was employed to remove any surface contamination produced by the rolling. The rolled foils were chemically thinned to the final desired thickness. In order to increase the residual resistance ratio (RRR) and make it possible to detect CESR in these samples, annealing in an oxygen atmosphere was essential.[11] After this treatment the samples had a measured RRR of 140 and 780 for the 4- and 11.1-$\mu$m sample, respectively, which corresponds to bulk RRR values of 740 and 16 700, respectively, if one assumes diffuse scattering at the sample surface.[12]

The sample thicknesses chosen here, which appear to be rather thin compared to Cu CESR samples[2,6] used elsewhere, were selected to give a favorable signal-to-noise ratio.[13] Furthermore, it was concluded from measurements at 21 GHz on samples with thickness $d \geqslant 20 \mu$m, that the 11.1-$\mu$m foil behaved like a "thick" sample which assured us that the typical bulk CESR properties were not masked by the rather small thickness of the sample, in agreement with previous results on Al.[5]

 

### B. Experimental results and discussion

#### *1. Linewidth*

The results presented here were obtained with reflection spectrometers working at frequencies of 9.27, 21, and 59.6 GHz. Linewidth data in the temperature range 4.2 to 50 K are shown in Fig. 1. These linewidths together with the $g$ values were deduced from experiments using careful line-shape fitting. The $A/B$ value obtained at 4.2 K is $3.4 \pm 0.2$ which is in good agreement with Dyson's theory as rewritten by Pifer and Magno.[14,15] Several unusual features can be seen from Fig. 1. $\Delta B$ for higher frequencies shows an increase in linewidth to a residual value $\Delta B_{res}$ as $T$ decreases. The magnitude of $\Delta B_{res}$, and the temperature at which the linewidth reaches its minimum depends on the measurement frequency and the sample. At 9.27 GHz no dip was observed in either sample while at 21 GHz only a shallow dip of about 0.25 mT was observed at 17 K for the 11.1-$\mu$m foil. The 59.6 GHz data shows the dip phenomenon in both samples although the effect is much weaker in the 4-$\mu$m sample; the minimum in linewidth at 59.6 GHz occurs at about 25 K. Another important feature to be noted from Fig. 1 is the fact that the linewidth values measured at different frequencies do not seem to join in the phonon-dominated regime ($T > 25$ K), which suggests the linewidth is also $f$ dependent in this high-$T$ region. To further investigate this $f$ dependence, we plot $\Delta B$ against $f$ for two temperatures, see Fig. 2(a), from which it can be concluded that in the range $T > 25$ K, $\Delta B$ is linearly dependent on frequency to the same extent for both samples. Comparing the $\Delta B$ results obtained on the 4-$\mu$m sample at 9.27 and 21 GHz, for which no dip occurs, one can see that this linearly frequency-dependent term is also present at low temperatures. As such, similar with interpretations on other metals[9] we can describe the observed total linewidth of Cu as

$$\left(\frac{1}{\gamma T_2}\right)_{\text{total}} = \Delta B_{\text{total}} = \Delta B_i + \Delta B_p + \Delta B_s + \alpha f + \Delta B_a(f,T) \ , \quad (1)$$

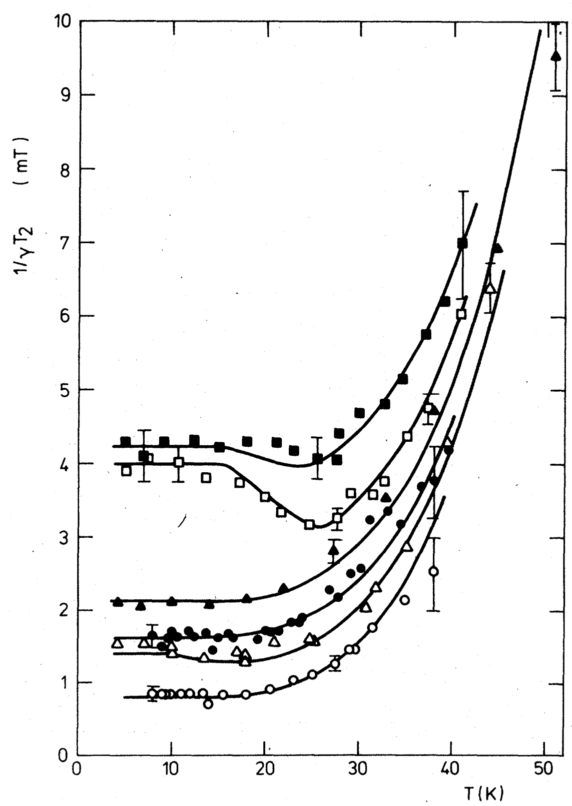


FIG. 1. Conversion factor corrected linewidths as a function of temperature at three frequencies for two copper foils. The open symbols represent data from a 11.1-$\mu$m foil and the solid ones stand for a 4-$\mu$m sample; ○●: 9.27 GHz; △▲: 21 GHz; □■: 59.6 GHz. The solid lines represent the linewidths calculated from Eq. (5).

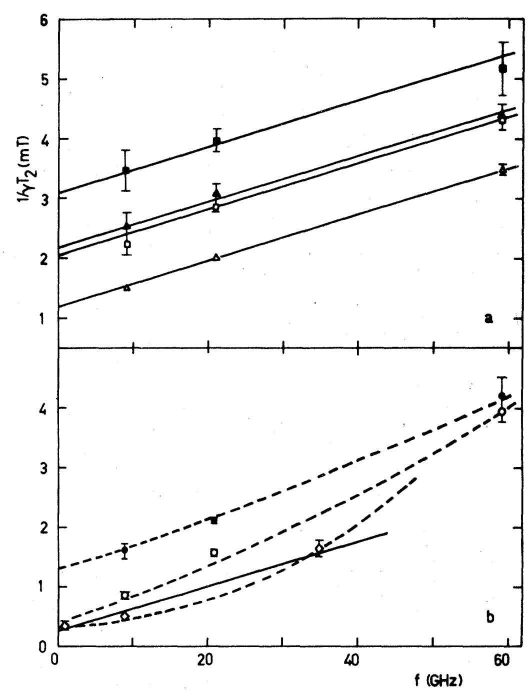


FIG. 2. Linewidth against frequency is plotted in (a) at two temperatures for two copper samples; △▲: 30 K; □■: 36 K. (b) gives the residual linewidths against frequency for the two samples. The diamonds are data from Ref. 6 measured on a 50-$\mu$m thick, single-crystal plate, and the dashed lines are parabolic fits to the experimental data. Open and solid symbols represent the data from 11.1 and 4-$\mu$m thick foils, respectively. The fitted solid lines in both figures have a slope of 0.040 +0.002 mT/GHz.

where $\Delta B_i$ is the linewidth due to impurity and defect spin-flip scattering, supposed to be $T$ and $f$ independent. $\Delta B_s$ is a $f$-independent term due to surface scattering, given in our case ($d << \delta_e$) by Dyson's result,[14,16]

$$\Delta B_s = \frac{\epsilon v_F}{d\gamma} \quad , \tag{2}$$

where $v_F$ is the Fermi velocity, $\epsilon$ is the electron spin-flip probability per surface collision, and $\delta_e$ is the spin depth; $\delta_e = (\frac{2}{3} v_F \lambda T_2)^{1/2}$, where $\lambda$ is the electron mean free path and $T_2$ is the electron-spin relaxation time. $\Delta B_p$ is the phonon contribution and $\alpha f$ is the term linearly proportional to $f$, which appears to be $T$ independent. Finally $\Delta B_a(f,T)$ is the term which describes the rise in the linewidth as $T$ decreases, and which is $f$ and $T$ dependent. In an earlier interpretation of results from copper,[6] this term was believed to be due to BMN related to the $g$ anisotropy over the Fermi surface and which is therefore given by

$$\Delta B_a(f,T) = \Delta B_{\rm BMN} = \frac{1}{\gamma}\left[\frac{\sigma_g}{\bar{g}}\omega\right]^2 \tau \quad , \tag{3}$$

if

$$(\sigma_g/\bar{g})\omega\tau << 1 \quad ,$$

where $\sigma_g$ is the mean $g$ spread over the Fermi surface, $\gamma$ is the gyromagnetic ratio, and $\tau$ is an electron collision time appropriate for the motional narrowing argument and which is usually assumed equal to $\tau_\rho$, the resistivity scattering time.

We will now elaborate further upon each of the proposed contributions to the total linewidth and try to determine to what extent each of these terms contributes to the total linewidth. One can easily deduce $\Delta B_p$ from $\Delta B_{\rm total}$. For the 9.27 GHz results from both samples and the 21 GHz results from the 4-$\mu$m sample one can put

$$\Delta B_p(f) = \Delta B_{\rm total}(f) - \Delta B_{\rm res}(f) \quad ,$$

as one notes that $\Delta B_{\rm res}$ is not troubled by a $\Delta B_a(f,T)$ term, and all other terms in $\Delta B_{\rm total}$ are assumed to be $T$ independent. This supposition is confirmed below by the smallness of the $\Delta B_a(f,T)$ term in these cases. For the 59.6 GHz measurements and the 21 GHz data from the 11.1-$\mu$m sample, one takes

$$\Delta B_p = \Delta B_{\rm total} - [\Delta B(T=T_d) - \Delta B_p'(T=T_d)] \quad .$$

Here $T_d$ is the temperature where the linewidth reaches its minimum and $\Delta B_p'(T=T_d)$ is the phonon contribution at this temperature deduced from the data obtained at the lowest frequency. The phonon contribution determined as such is shown in Fig. 3 for the thicker sample. It can be seen that within the experimental error the $\Delta B_p$ term is identical at the

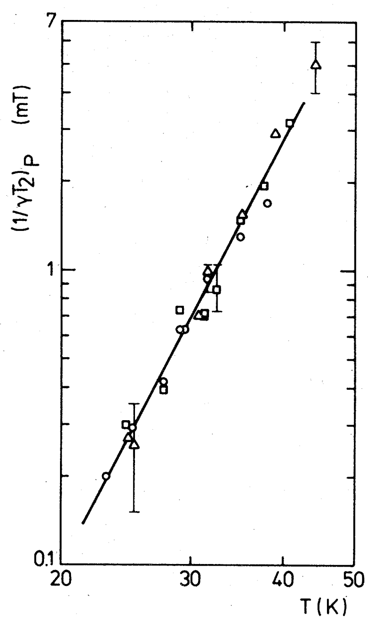


FIG. 3. Phonon-dependent part of the linewidth $\Delta B_p$ as a function of temperature at three frequencies for a 11.1-$\mu$m thick 99.999% pure copper foil: ○: 9.27 GHz; Δ: 21 GHz; □: 59.6 GHz. This plot indicates that $\Delta B_p$ is equal at the three frequencies. The solid line is a least-square fit of the data between 23 and 41 K, and is given by $\Delta B_p = 1.3\times 10^{-7} T^{4.6\pm 0.25}$ mT.

three frequencies. The least-squares fit represented by the solid line in Fig. 3 gives

$$\Delta B_p = 1.3\times 10^{-7} T^{4.6\pm 0.25} \text{ mT} \quad , \tag{4}$$

in accordance with earlier observations reported in the literature.[17] Within the experimental errors the same $\Delta B_p$ term was found for the 4-$\mu$m sample.

Now returning to the $\alpha f$ term, the value of $\alpha$ averaged over $T$ is $\alpha = 0.040 \pm 0.002$ mT/GHz for both samples; this is demonstrated at 30 and 36 K in Fig. 2(a). From this plot one also obtains $\Delta B_s + \Delta B_i$. The intercepts of the straight lines in Fig. 2(a) with the $\Delta B$ axis should represent $\Delta B_i + \Delta B_s + \Delta B_p$ at the marked temperatures. Subtracting off $\Delta B_p$ given by Eq. (4) gives for $\Delta B_s + \Delta B_i$ the mean values of $0.40 \pm 0.08$ and $1.31 \pm 0.1$ mT for the 11.1 and 4-$\mu$m sample, respectively. It is not realistic to try to extract an $\epsilon$ value from a comparison between these two samples using the $d^{-1}$ dependence of $\Delta B_s$, given by Eq. (2). However, we note that if one assumes that the whole of the $\Delta B_s + \Delta B_i$ contribution deduced from this interpretation is caused by surface relaxation, one finds that $\epsilon \lesssim 10^{-3}$, which is smaller than the values reported elsewhere.[18]

One now can deduce the frequency and temperature dependence of

$$\Delta B_a(f,T) = \Delta B_{\rm total} - (\Delta B_p + \Delta B_i + \Delta B_s + \alpha f) \quad .$$

It is found that $\Delta B_a$ does not depend on $T$ below

13 K and decreases almost linearly to zero at 26 K for 59.6 GHz; these temperature values shift to somewhat lower values for the lower frequencies. Fig. 2(b) is a $\Delta B_{res}$ against $f$ plot for both samples; while the thicker sample data fit a straight line very well within the experimental errors, the thinner sample fits better to an $f^2$ dependence and in view of previous interpretations,[1] the latter dependence will be fitted. The fitted solid lines represent curves of $\Delta B_i + \Delta B_s + \alpha f + \beta f^2$, with $\beta = 1.3 \times 10^{-4}$ and $3.5 \times 10^{-4}$ mT/GHz$^2$ for the 4 and 11.1-$\mu$m sample, respectively. Note that these fits do give intercepts on the $\Delta B$ axis which give values of $\Delta B_i + \Delta B_s$ in accordance with the values deduced from Fig. 2(a). Figure 2(b) also contains Lubzens and Schultz's[6] values of $\Delta B_{res}$ for a 50-$\mu$m thick single-crystal sample, together with the parabolic fit proposed by them. It is clear that this parabola is too steep for our experimental results from the 11.1-$\mu$m sample, which in view of the reported RRR values[2] has about the same $\tau_p$ value as their 50-$\mu$m sample. Putting, as usual $\tau = \tau_p$, from Eq. (3) we find that $\sigma_g/\bar{g} \simeq 0.009$ and 0.008 for the 4 and 11.1-$\mu$m sample, respectively, which values are indeed smaller than the one deduced by Lubzens *et al.*[1] ($\sigma_g/\bar{g} \simeq 0.013$).

It is surprising that these authors do not find a dip in the $\Delta B(T)$ plot at 35 GHz in a 50-$\mu$m-thick sample since a dip was observed at 21 GHz in the 11.1-$\mu$m foil. This suggests that their $\Delta B_{res}$ data did not contain much of the $\Delta B_a(f,T)$ term, in which case a straight-line fit through their points should give the $\alpha f$ term originating from our experimental data, which is indeed the case [see Fig. 2(b)]. Moreover they do not see an $\alpha f$ contribution in the phonon-dominated regime; this may be due to their low signal-to-noise ratio in this $T$ region, the errors associated with the background signals or the smaller frequency range available,[2] all of which might have obscured the $\alpha f$ term.

It should also be noted that by fitting either a linear or parabolic $f$ dependence to our 11.1-$\mu$m sample data, one finds that $\Delta B_i + \Delta B_s$ is only about 0.1 mT wider than the corresponding quantity of their 50-$\mu$m single-crystal sample and it is very likely that the first sample has a bigger $\Delta B_s$ content so that we may conclude our thick foil to be at least as pure as the 50-$\mu$m sample. This accords with their reported RRR value[2] of 1000.

From this analysis we find that $\Delta B_{total}$ for our copper samples is given by

$$\Delta B_{total}(d = 4\mu\text{m}) = (1.31 \pm 0.1) + 1.3 \times 10^{-7} T^{4.6 \pm 0.25} + (0.040 \pm 0.002) f + 1.3 \times 10^{-4} f^2 \text{ mT} ,$$

and (5)

$$\Delta B_{total}(d = 11.1\mu\text{m}) = (0.40 \pm 0.08) + 1.3 \times 10^{-7} T^{4.6 \pm 0.25} + (0.040 \pm 0.002) f + 3.5 \times 10^{-4} f^2 \text{ mT} ,$$

where $f$ is expressed in GHz. The theoretical linewidths calculated from Eq. (5) are plotted in Fig. 1 as the solid lines which show very good agreement with the experimental data.

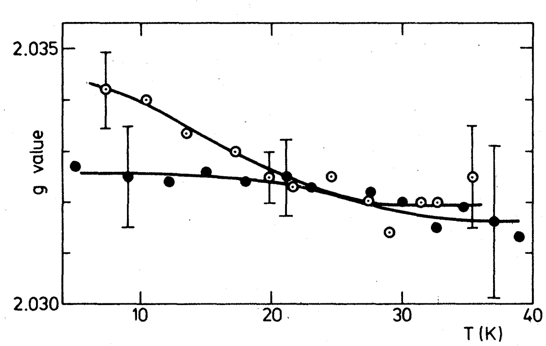


FIG. 4. $g$ factor at 59.6 GHz plotted against temperature for two copper foils. The solid and open circles stand for data taken on a 4 and 11.1-$\mu$m thick foil, respectively.

### 2. *g value*

The $g$ value was found to be constant, within experimental error, over the whole range $4.2 < T < 50$ K, both at 9.27 and 21 GHz. The averaged values are given by $2.0328 \pm 0.001$ and $2.03325 \pm 0.0003$ at 9.27 and 21 GHz, respectively. These averaged values agree with other published results.[1,6] As shown in Fig. 4, the $g$ value at 59.6 GHz however increases slightly as $T$ decreases below 30 K, the increase being more pronounced for the 11.1-$\mu$m sample. This agrees with the view that if the $g$ increase is related to the $\beta(T) f^2$ term in the linewidth, then the $\beta(T)$ of the 4-$\mu$m sample is smaller than that of the 11.1-$\mu$m sample one, as found above.

## III. SUMMARY

In this paper we have shown that the CESR linewidth of pure copper, as well as in aluminum, contains an $\alpha f$ term which is found to be temperature independent as found previously[9] for aluminum. A further frequency-dependent term appears only at low temperature and is probably proportional to $f^2$, although because of the uncertainties in the data we cannot preclude a fit which is merely linearly dependent on $f$. If the former conclusion is correct then the $\beta(T)f^2$ term in the linewidth and the associated $g$ shifts observed can, in view of the measured $\tau_\rho$ values of our samples, still be explained by a simple partial breakdown of motional narrowing argument taking into account the $g$ spread of the conduction electrons over the Fermi surface. However, now the magnitude of the BMN term is much smaller than proposed in earlier work.[6] Finally we note that the general expression for the linewidth of the CESR of copper is very similar to that reported elsewhere for aluminum[9] and is once again at variance with that normally accepted.

## ACKNOWLEDGMENTS

We acknowledge fruitful and stimulating discussions with Dr. R. Sambles and Dr. J. Cousins, University of Exeter, England and Dr. J. Witters, University of Leuven, Belgium. S. P. B. acknowledges the Science Research Council for the provision of a maintenance grant. A. S. is grateful to the *National Fonds voor Wetenschappelijk Onderzoek*, Belgium, for financial support.

---

[1]D. Lubzens, M. R. Shanabarger, and S. Schultz, Phys. Rev. Lett. 29, 1387 (1972).

[2]For experimental data see M. R. Shanabarger, thesis (University of California, 1970) (unpublished); and D. Lubzens, thesis (University of California, 1975) (unpublished).

[3]D. R. Fredkin and R. Freedman, Phys. Rev. Lett. 29, 1390 (1972).

[4]L. Janssens, A. Stesmans, J. Cousins, and J. Witters, Phys. Status Solidi B 67, 231 (1975).

[5]J. R. Sambles, G. Sharp-Dent, J. E. Cousins, A. Stesmans, and J. Witters, Phys. Status Solidi B 79, 645 (1977).

[6]D. Lubzens and S. Schultz, Phys. Rev. Lett. 36, 1104 (1976).

[7]R. Dupree and B. W. Holland, Phys. Status Solidi 24, 275 (1967).

[8]G. L. Dunifer and M. R. Pattison, Phys. Rev. B 14, 945 (1976); J. van Meijel, A. Stesmans and J. Witters, Solid State Commun. 21, 753 (1977).

[9]J. R. Sambles, J. E. Cousins, A. Stesmans, and J. Witters, Solid State Commun. 24, 673 (1977).

[10]The 99.999% pure polycrystalline rod was obtained from Materials Research Corporation, New York. The other material was a 99.9996% polycrystalline ingot from Koch-Light Ltd, England.

[11]F. R. Fickett, Mater. Sci. Eng. 14, 199 (1974).

[12]E. Ditlefsen and J. Lothe, Philos. Mag. 14, 759 (1966).

[13]A. Stesmans, J. van Meijel, and J. Witters, J. Phys. F 7, 199 (1977).

[14]F. J. Dyson, Phys. Rev. 98, 337 (1955).

[15]J. H. Pifer and R. Magno, Phys. Rev. B 3, 663 (1971) and references therein.

[16]M. B. Walker, Phys. Rev. B 3, 30 (1971).

[17]A least-squares fit to the data of M. R. Shanabarger and D. Lubzens (see Ref. 2) over the same $T$ range as covered in our Fig. 3 (i.e. $23 < T < 41$ K) shows their $\Delta B_p$ to be proportional to $T^{4.7 \pm 0.3}$.

[18]R. Meservey and P. M. Tedrow, Phys. Rev. Lett. 41, 805 (1978) and references therein.