Comment on anomalous nuclear-acoustic-resonance line shapes in Ta with mobile hydrogen impurities*

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We have performed detailed numerical calculations for nuclear-acoustic-resonance line shapes appropriate for Ta where the spin relaxation is dominated by mobile hydrogen impurities. These calculations include intraspin cross relaxation due to defect-generated static electric field gradients. The calculated line shapes show a large amount of structure and are in almost complete quantitative agreement with recent experimental results.

Nuclear acoustic resonance (NAR) can provide a powerful tool in the study of point defects in crystals and in the study of the motion of interstitial hydrogen in metals. Recently we have developed theories of spin relaxation due to mobile hydrogen impurities[1] and the effects of intraspin cross relaxation[2] due to static electric field gradients on magnetic-resonance line-shape functions. In this paper we present the results of detailed calculations using these theories and compare them with the results of recent experiments[3-5] on Ta with hydrogen impurities. We believe that the excellent agreement between theory and experiment on line shapes with such a large amount of structure shows that quantitative studies of defects can be made using magnetic-resonance techniques.

In addition, Swendsen and Kehr[6] have performed calculations of the dynamic field gradient correlation functions for hydrogen in bcc metals and have applied their results to hydrogen in Ta. They find a considerable anisotropy in these field gradient correlation functions which implies a measurable anisotropy in the NAR linewidths. They use the results of their calculation to explain the observed ratio between the NAR $m=1$ and $m=2$ linewidths in Ta.[5] However, we wish to point out that careful measurements of these linewidths showed no angular dependence.[4] Further, in this note, we show that the ratio between the two observed linewidths can be completely explained by our theory under the assumption of isotropic dynamic field gradient correlation functions.

The basic equations for the line-shape functions described in this paper have been previously published. In Ref. 1 we derive expressions for the relaxation rates of the spin multipole modes (l, m) due to the dynamic electric field gradients generated by mobile hydrogen impurities. If we assume that the dynamic field gradient correlation functions are spherically symmetric, then the multipole relaxation rates $\Gamma_{l,m}$ depend only on l and not on m and can thus be denoted by Γ_l. Their ratios are rather easily deduced, and for the case of $I=\frac{7}{2}$, appropriate to Ta, one obtains[7] $\Gamma_2=2.8\Gamma_1$, $\Gamma_3=5\Gamma_1$, $\Gamma_4=7\Gamma_1$, $\Gamma_5=8\Gamma_1$, $\Gamma_6=7\Gamma_1$, and $\Gamma_7=2.8\Gamma_1$. Thus in the absence of any other mechanisms NMR measurements which couple to the spins' dipole ($l=1$) moment would yield a Lorentzian line with a linewidth Γ_1 (in frequency units) and NAR measurements which couple to the spins' quadrupole ($l=2$) moment would yield Lorentzian lines with linewidth $\Gamma_2=2.8\Gamma_1$. That is, the NAR $m=1$ and NAR $m=2$ line shapes would be identical (as a function of frequency).

However, obtainable single crystals of Ta appear to always contain appreciable static electric field gradients. Since the intrinsic relaxation of the spins is controlled by an exponential mechanism, the effects of the static electric field gradients can be taken into account exactly[2] if we know their distribution. We shall assume a Lorentzian distribution of static electric field gradients with a Lorentzian width ω_q characterizing an average shift of the energy level m by the amount $m^2\omega_q$. This distribution is appropriate for field gradients due to charge-point defects.[8] The existence of these static electric field gradients breaks the spherical symmetry assumed earlier and is responsible for the differences between the NAR $m=1$ and NAR $m=2$ line shapes.

We have numerically computed the line shapes for the spin modes $(l=2, m=2)$ and $(l=2, m=1)$ appropriate to the NAR $m=2$ and NAR $m=1$ experiments, respectively, using the equations outlined in Ref. 2. Since the line shapes depend rather drastically on the dimensionless ratio ω_q/Γ_1, it is impossible to present a figure of a general line shape. Thus since most experiments measure the derivative of the absorption rather than the absorption itself, we display our results as the position (in frequency) of absorption extrema (minima and maxima) as a function of ω_q/Γ_1. Since the derivative lines are antisymmetric about the resonance frequency, the position of the extrema are measured from the center of the line

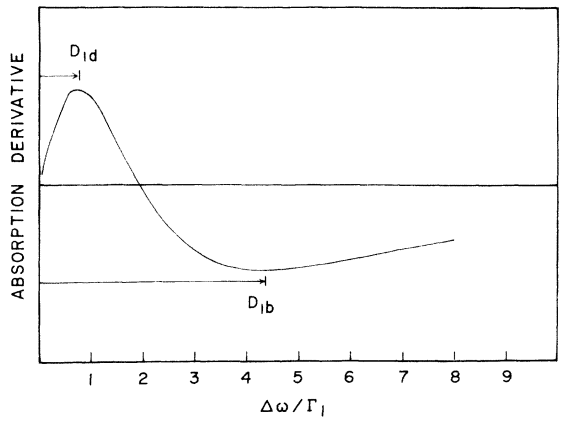

FIG. 1. A typical NAR $m=1$ derivative absorption spectrum. This example is for $\omega_q/\Gamma_1=1$.

in the direction of increasing frequency. Although one normally expects only one derivative minimum and no derivative maxima, this is not the case here because of intraspin cross relaxation.[2] For the NAR $m=1$ line shape in general there are both a maximum and a minimum in the absorption derivative as shown in Fig. 1. The derivative maximum corresponds to a dip in the absorption spectra. Using the language of Ref. 5 we let D_{1d} equal the distance in frequency (from the center of the line) of the $m=1$ first derivative maximum divided by Γ_1 and D_{1b} equal the distance of the $m=1$ first derivative broad minimum divided by Γ_1. The derivative of the NAR $m=2$ spectra may have either one or two minima. The distance to the first minima divided by Γ_1 is denoted by D_{2n} (n for narrow) and the distance to the second (if it exists) is denoted by D_{2b} (b for broad).

Results of our calculations are displayed in Fig. 2 and 3, which display D_{1d}, D_{1b}, D_{2n}, and D_{2b} as functions of ω_q/Γ_1. For small field gradients the NAR $m=1$ derivative line has only a minimum and acquires the maximum only if $\omega_q > 0.2\Gamma_1$. Similarly the NAR $m=2$ derivative line acquires a second minimum only if $\omega_q > 13\Gamma_1$. We further note that D_{1d} and D_{2n} are roughly independent of ω_q, while D_{1b} and D_{2b} are roughly proportional to ω_q for large ω_q. Since D_{1b} and D_{2n} are often used to compare the two NAR lines, their ratio is also plotted in Figs. 2 and 3.

We shall now compare these results to the experimental results of Ströbel, Läuger, and Bömmel in Ref. 5. The comparison is made at temperatures between 200 and 250 K where we are certain that the intrinsic decay mechanism of

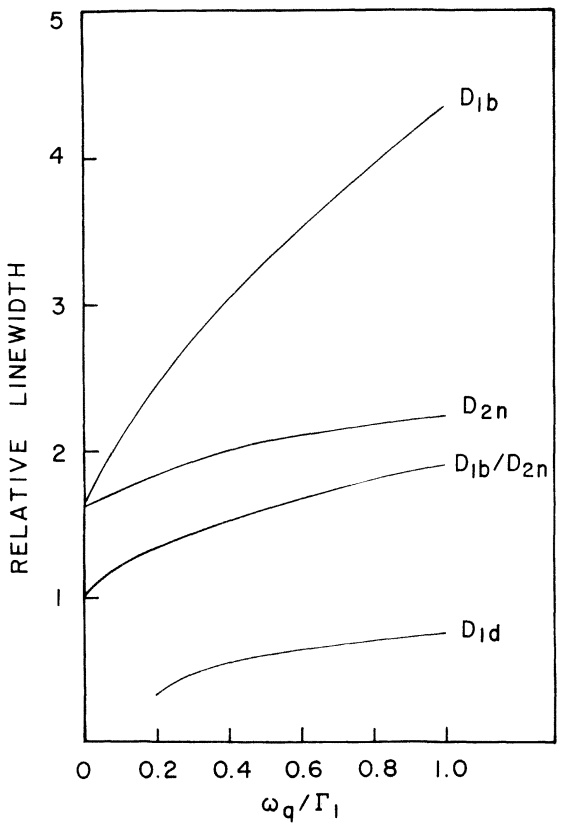

FIG. 2. Positions of NAR $m=1$ and $m=2$ absorption derivative extrema for $\omega_q < \Gamma_1$. The D's are defined in the text.

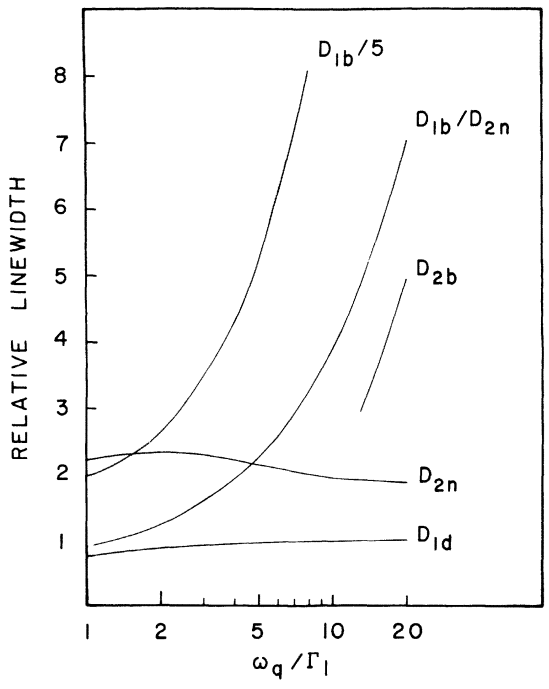

FIG. 3. Positions of NAR $m=1$ and $m=2$ absorption derivative extrema for $\omega_q > \Gamma_1$. The D's are defined in the text.

TABLE I. Experimental and theoretical linewidths for the NAR $m=1$ and NAR $m=2$ line shapes in Ta.

Temperature (K)	200	217	233	250
$m=2$ linewidth in gauss (experimental)	200	140	100	73
$m=1$ broad linewidth in gauss (experimental)	700	500	454	414
$m=1$ broad linewidth in gauss (theoretical)	664	605	444	359
$m=1$ dip linewidth in gauss (experimental)	120	86	66	60
$m=1$ dip linewidth in gauss (theoretical)	124	90	70	57
ω_q/Γ_1	0.70	0.80	1.45	2.3

the spins is dominated by the mobile hydrogen impurities. The results of the comparison are given in Table I. The measured linewidth of the NAR $m=2$ resonance was assumed as input and a single value of ω_q for all temperatures was chosen to give the best fit. We then used the results in Figs. 2 and 3 to obtain the rest of the linewidths keeping in mind that the NAR $\Delta m=2$ linewidth in frequency units is 2γ times its linewidth in magnetic field units. The experimental points were read off of Fig. 2 of Ref. 5.

We see that the agreement between theory and experiment is at worst about 15%, which is probably no more than the accuracy with which data can be read from the figure in Ref. 5. The ratio (in frequency units) of D_{1b}/D_{2n} over this temperature interval ranges from 1.75 to 2.84. Since this ratio would have been one if no static electric field gradients had been present, it is a measure of the importance of intraspin cross relaxation and not a measure of the anisotropy of the dynamic field gradient correlation functions. We further note that while the results in this paper do depend on isotropic dynamic field gradient correlation functions, they do not depend on the static electric field gradients characterized by ω_q being isotropic. Thus the results can be applied to some systems with anisotropic line shapes.

Finally, one might ask why Swendsen and Kehr's results yield such anisotropic dynamic field gradient correlation functions which are in disagreement with experimental results. Although we do not know the reason for the disagreement, we would like to point out a number of seemingly reasonable assumptions in their calculation which cannot be rigorously justified. There are 24 nearest-neighbor tetrahedral sites for a hydrogen nucleus to jump to. They assume, as is usually done, that the jump rate to each of these is identical, although these sites are not crystallographically equivalent. Further, although screening has been neglected in these calculations, this is not necessarily justified and the screening may itself be anisotropically dependent on the crystallographic position of the tetrahedral sites. Finally, it may be that it is necessary to include jumping rates to next-nearest-neighbor sites.

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