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NMR Line Broadening in Solids by Slowing Down of Spin Fluctuations

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The ^{109}Ag nuclear magnetic resonance line in a sample of polycrystalline AgF is observed to broaden substantially when the ^{19}F spins are irradiated near the magic angle in their rotating frame. This is due to the reduction of $^{19}F-^{19}F$ dipolar coupling, which normally causes fluctuations in the $^{19}F-^{109}Ag$ interactions (Abragam and Winter), inducing an exchange narrowing analogous to classical motional narrowing. The ^{109}Ag linewidths obtained over the entire motional range at different ^{19}F frequencies are compared with those calculated exactly from the ratio of second to fourth moment.

The phenomenon of motional narrowing is very common in magnetic resonance [1, 2]. Starting from a rigid solid in which the resonance lines are broadened by static magnetic interactions between the spins, the sample is heated and, as rapid thermal molecular reorientation and translations ensue, the lines narrow until high resolution spectra typical of isotropic fluids are observed. An interesting fact, shown by van Vleck [3] and more comprehensively by Anderson and Weiss [4] is that there is another form of motional narrowing which may be thought of as occurring entirely in spin space without thermal motion. This can occur if there are exchange interactions which commute with the magnetization operator but not with the perturbation interaction responsible for the line broadening. The exchange induces rapid "flip-flops" of nuclear spins which can average away the broadening interactions if the exchange is strong enough. As a particular example of considerable current interest, consider the case of the ^{109}Ag resonance in AgF first observed by Abragam and Winter [2, 5]. The line is unusually narrow for a solid and this is explained by the rapid decoupling of $^{109}Ag-^{19}F$ dipolar interactions by the $^{19}F-^{19}F$ dipolar couplings. The effect is marked since $\gamma_F \gg \gamma_{Ag}$ and the qualitative analogy with thermal motional narrowing is evident. To date, however, the analogy has not been complete. Whereas in the case of classical motional narrowing the rate of fluctuations can be controlled and the full regime from rigid to motionally narrowed can be covered by variation of temperature, no such control has been exercised over spin fluctuations in AgF. In particular if it were possible to eliminate the $^{19}F-^{19}F$ coupling, Abragam has predicted that the ^{109}Ag resonance should broaden, allowing the full rigid lineshape to be observed in analogy to thermal cooling. Similar reasoning has been applied to dipolar oscillations and spectra by Waugh and coworkers [6].

In this letter, we demonstrate for the first time a completion of the analogy between spin and thermal fluctuations by selectively reducing the ^{19}F spin fluctuations. Figure 1 shows the observed behavior. When the ^{19}F spins in a sample of polycrystalline AgF are irradiated with a strong radiofrequency field such that the effective field in the rotating frame is close to the magic angle, the $^{19}F-^{19}F$ dipolar interactions are reduced [7] *and the ^{109}Ag resonance is indeed observed to broaden.* A continuous variation of the spin fluctuation rate between the limiting cases of extreme narrowing and rigid is at the experimenters control and is discussed in the following. We consider an S spin system, with gyromagnetic ratio γ_S where dipolar interactions among the S spins are neglected is coupled to an abundant I spin system with gyromagnetic ratio γ_I placed in a static magnetic field H_0. A strong rf field is applied close to the Larmor frequency ω_{0I} of the I spins, with

$$\mathcal{H}_{1I} = 2\omega_{1I} I_x \cos \omega_I t. \tag{1}$$

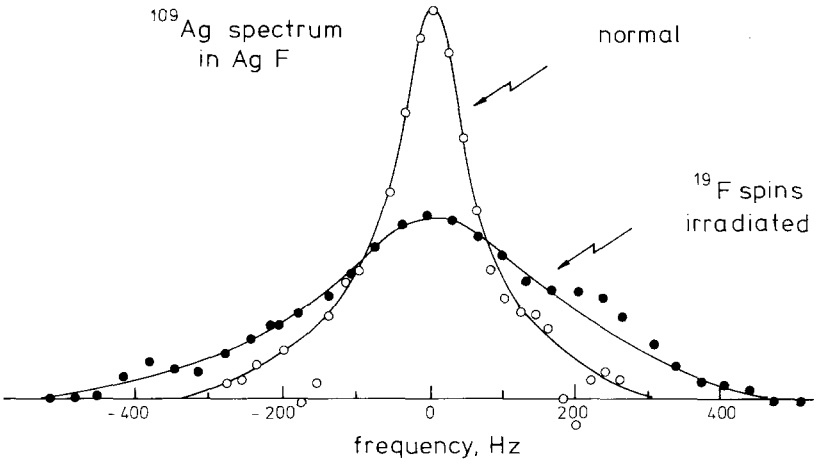

Fig. 1. Silver (^{109}Ag) resonance line at 4.2 MHz in polycrystalline AgF with and without irradiation of the ^{19}F spins. Irradiation of the ^{19}F spins is performed with an rf field of 14 G close to the magic angle in their rotating frame. The scaling factor $\cos\vartheta_I$ has been taken into account in drawing the frequency scale

It is convenient to express the Hamiltonian of the spin system in a "tilted doubly rotating frame" (DTR): represented by the transformation DTR [8]

$$R = e^{-i(\omega_I I_z + \omega_{0S} S_z)t} \tag{2}$$

with

$$T = e^{i\vartheta_I I_y} \tag{3}$$

and

$$D = e^{-i\omega_{eI} I_z t} \tag{4}$$

where

$$\tan\vartheta_I = \omega_I/(\omega_{0I} - \omega_I)$$

and

$$\omega_{eI} = [(\omega_{0I} - \omega_I)^2 + \omega_{1I}^2]^{1/2}. \tag{5}$$

The total Hamiltonian in the DTR frame neglecting time dependent terms is given by:

$$\mathcal{H} = \mathcal{H}_{II} + \mathcal{H}_{IS} \tag{6}$$

with

$$\mathcal{H}_{II} = P_2(\cos\vartheta_I) \cdot \mathcal{H}_{II}^{(0)} \tag{7a}$$

$$\mathcal{H}_{IS} = \cos\vartheta_I \mathcal{H}_{IS}^{(0)} \tag{7b}$$

and $\mathcal{H}_{II}^{(0)}$ and $\mathcal{H}_{IS}^{(0)}$ are the unperturbed dipolar interactions among the I spins

$$\mathcal{H}_{II}^{(0)} = \sum_{i<j} A_{ij}(3I_{zi}I_{zj} - \mathbf{I}_i \cdot \mathbf{I}_j) \tag{8}$$

and between the I and S spins

$$\mathcal{H}_{IS}^{(0)} = \sum_j 2B_j I_{zj} S_z \tag{9}$$

A_{ij} and B_j are geometrical parameters and have their usual meaning. We see that $\mathcal{H}_{II}$ in (7) scales as $P_2(\cos\vartheta_I)$, when the frequency of the rf field is varied, whereas the I-S interaction $\mathcal{H}_{IS}$ is scaled as $\cos\vartheta_I$!

This gives experimental control over the ratio of these interactions.

The physical picture is that $\mathcal{H}_{IS}$ normally induces a broadening of the S resonance. However, fluctuations in $\mathcal{H}_{IS}$ caused by $\mathcal{H}_{II}$ can cause a narrowing of the resonance line. This can be described using the approach of McArthur, Hahn and Walstedt [9] who use an Anderson-Weiss theory for the effect of $\mathcal{H}_{II}$ on $\mathcal{H}_{IS}$. The normalized S free induction decay is given by:

$$S(t) = \exp\left\{-M_2^{IS}\int_0^t dt'(t-t')\,a(t')\right\} \tag{10}$$

where M_2^{IS} is the S second moment due to $\mathcal{H}_{IS}$ and $a(t)$ is the correlation function for fluctuations in $\mathcal{H}_{IS}$

$$a(t) = \mathrm{Tr}\{\mathcal{H}_{IS}(t)\mathcal{H}_{IS}\}/\mathrm{Tr}\{\mathcal{H}_{IS}^2\} \tag{11}$$

where

$$\mathcal{H}_{IS}(t) = e^{-i\mathcal{H}_{II}t}\,\mathcal{H}_{IS}\,e^{i\mathcal{H}_{II}t}. \tag{12}$$

Since all odd moments of $a(t)$ vanish, the correlation time τ for the fluctuations of $\mathcal{H}_{IS}$, can be expressed by the second moment N_2 of $a(t)$ as

$$\tau = (N_2/2)^{-1/2} \tag{13}$$

which readily results in

$$\tau = |P_2(\cos\vartheta_I)|^{-1} \cdot \tau_c \tag{14}$$

where τ_c is the correlation time for no irradiation ($\vartheta_I = 0$). Using the standard notation for moments [2], τ_c is according to Equation (13) given by the ratio of fourth to second moment as

$$\tau_c = [M_4^{II\,IS}/2 \cdot M_2^{IS}]^{-1/2}. \tag{15}$$

Exactly as in the classical BPP theory and the Anderson-Weiss theory the parameter determining which regime we are in depends on the product of the cor-

relation time of the fluctuations and the rigid S linewidth $\Delta\omega$, i.e. from (7b) and (14)

$$\Delta\omega\tau=\frac{\cos\vartheta_I}{|P_2(\cos\vartheta_I)|}\cdot(M_2^{IS})^{1/2}\cdot\tau_c \tag{16}$$

when $\Delta\omega\tau\gg1$ we are in the rigid limit and when $\Delta\omega\tau\ll1$ we have extreme motional narrowing for the S spins. Since the trigonometric factor in Equation (16) is at our experimental control, we can cover the entire regime, providing of course $(M_2^{IS})^{1/2}\tau_c$ is small enough. For polycrystalline AgF we calculate exactly $\tau_c=$ 75.7 μsec and $(M_2^{IS})^{1/2}=405$ Hz, so this condition is clearly fulfilled.

The experimental results of ^{109}Ag linewidth at half height as a function of ϑ_I, i.e. as the ^{19}F frequency is varied, are shown in Figure 2. Since the form of the correlation function $a(t)$ is not calculably exactly, we can make no a priori comparison with theory. However, we can qualitatively discuss the behavior by using as the linewidth for the S spins

$$\delta=\frac{M_2^{3/2}}{M_4^{1/2}} \tag{17}$$

which is expected for a Lorentzian-like lineshape [2]. The moments in (17) are given in the case of the I irradiation by:

$$M_2=\cos^2\vartheta_I\cdot M_2^{IS}$$

$$M_4=P_2(\cos\vartheta_I)^2\cdot\cos^2\vartheta_I\cdot M_4^{II\,IS}+\cos^4\vartheta_I M_4^{IS\,IS}.$$

These moments were calculated exactly from the appropriate lattice sums for AgF and the calculated linewidth δ according to (17) is plotted in Figure 2 as the solid line, showing the observed increase in the ^{109}Ag linewidth. Note that the actual experimental and theoretical increase of S linewidth at the magic angle is $3^{1/2}$ times larger than shown in Figure 2 due to the factor $\cos\vartheta_I$ in $\mathcal{H}_{IS}$.

Two final comments are in order here. Firstly, note that neither expression (10) nor (17) (Gaussian and Lorentzian) are expected to be valid in the rigid regime, i.e. $P_2(\cos\vartheta_I)\simeq0$. In fact, the S lineshape at $\vartheta_I=54.7°$ were $\mathcal{H}_{II}=0$ can be calculated exactly for spin 1/2 and is given by:

$$S(t)=\prod_j\cos((\tfrac{1}{3})^{1/2}B_j t). \tag{18}$$

An exact computer simulation of (18) with a powder average for AgF shows indeed the lineshape is neither Gaussian nor Lorentzian. In fact the exact theoretical linewidth $\Delta\nu=\delta/\Pi$ is calculated to be $\Delta\nu=453$ Hz which is considerably larger than that in Figure 2. We attribute the fact that we do not observe such a large broadening at the magic angle to rf field inhomogeneity and non secular terms in the I coupling in the DTR frame due to the finite magnitude of H_1.

Secondly, we mention that we have also investigated other systems in this way. In particular the common case of $^{13}C-^1H$ has been studied and the ^{13}C resonance in polycrystalline adamantane was also found to be spin motionally narrowed, broadening by a factor of 2 on irradiation of the ^1H spins.

We believe that with the analogy we have drawn here between the freezing of thermal motion and the slowing down of spin fluctuations by rf irradiation, some advances can be made in the extraction of full rigid lineshapes for S spins in solids and the measurement of spin correlation function in the motional narrowing regime.

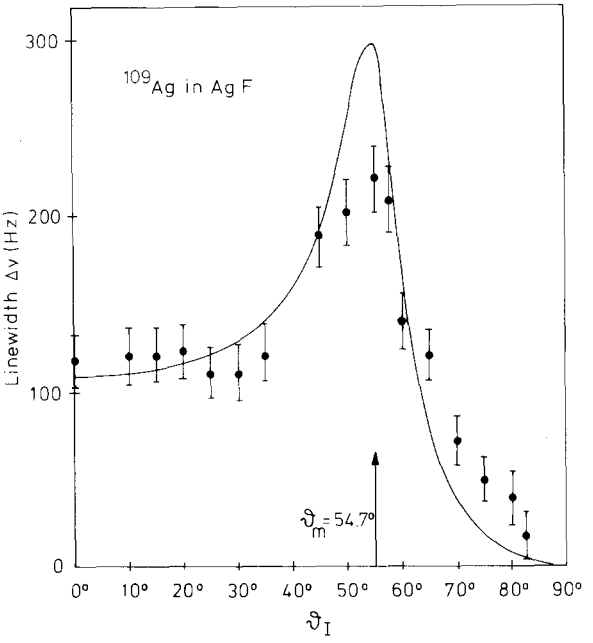

Fig. 2. Calculated (Eq. (17)) and experimental excess half width $\Delta\nu=\delta/\Pi$ of ^{109}Ag in polycrystalline AgF at 4.2 MHz under irradiation of the ^{19}F spins with an rf field of 14 G at the angle ϑ_I in their rotating frame. The experimental excess half width has been obtained by deconvolution of the experimental spectra with the totally fluorine decoupled ($\vartheta_I=\Pi/2$) silver resonance line

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