High Sensitivity Nuclear Quadrupole Resonance Approach for Detection of Modulation Wave Motion in Incommensurate Systems

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In contrast to conventional NMR techniques that use magnetic field gradients (MFG's) to detect the diffusion of moving atoms, we have developed a highly sensitive approach for detecting electric field gradient (EFG) fluctuations seen by stationary atoms. These EFG fluctuations were observed in the quadrupole perturbed NMR behavior of a stationary nucleus (^{93}Nb) in the incommensurate insulator barium sodium niobate and are attributed to motion of the modulation wave. We observed effective diffusion constants of order 10^{-13} cm^2/s, which are 4 orders of magnitude smaller than those currently detectable with MFG NMR.

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Since the early work of Hahn [1], nuclear magnetic resonance (NMR) has been one of the best techniques for studying self-diffusion of mobile nuclei. Slow translational diffusion can be observed in liquids and other systems of sufficiently narrow NMR linewidth by monitoring a change in the NMR frequency of a moving spin in a static magnetic field gradient (MFG) [2]. In this Letter we describe the first observations of similar effects for a stationary quadrupolar nucleus in a time varying electric field gradient (EFG). Specifically, our experiments were performed in an incommensurate solid where the variations in the EFG are produced by translational motion of the modulation wave. This approach contrasts to that used in the typical diffusion measurement [2] in which the interaction field (the MFG) is static but the nuclear position varies with time. In our experiment, the position of the observed nucleus is constant in time but the interaction field (in this case, the EFG) fluctuates.

It is shown here that extremely small diffusion coefficients can be measured by this new quadrupole-perturbed NMR technique. The diffusion effect shows up as a decay of the magnetization with an exponent proportional to the cube of time, similar to the decay observed in conventional MFG NMR. The sensitivity of this EFG technique for detecting random translational motions exceeds by more than 4 orders of magnitude the sensitivity obtainable by conventional MFG NMR. The physical reason for this is that the modulation wave in an incommensurate solid produces a much larger frequency variation over much smaller distances than are obtainable by conventional MFG's. Normally in a typical NMR diffusion experiment, field gradients of about 0.1 T/cm (corresponding to about 1–4 Hz variation over 100 Å) are used. Even with the large fringe fields of superconducting magnets [3] which produce gradients as large a 5 T/cm, the frequency variation over 100 Å will be only 200 Hz. The effective field gradient variation produced by the modulation wave in barium sodium niobate (BSN) is 20 kHz over 100 Å, which is 2 orders of magnitude larger. Furthermore, since the change in NMR signal is proportional to the square of this field gradient variation, the effective sensitivity is 4 orders of magnitude better than the best currently available with magnetic field gradient NMR. In particular, we observed effective diffusion coefficients as small as 10^{-13}–10^{-15} cm^2/s.

The NMR behavior resulting from fluctuating electric field gradients (and thus the NMR effects) which arise from a mobile modulation wave and are experienced by a stationary nucleus should be similar to those experienced by a mobile nucleus diffusing along a stationary modulation wave provided that the modulation wave's motion has sufficient range. If the modulation wave's motion is the result of local depinning, there will be large amplitude motions (which may be approximated as free diffusion) far from the pinning points and much smaller amplitude motions near the pinning points (which may be treated as restricted diffusion).

In addition to its greater sensitivity, this way of studying translational diffusion in solids offers new insights not obtainable either by conventional NMR or by non-NMR techniques. Hysteresis and metastability effects, such as dielectric and birefringence hysteresis [4] or x-ray broadening of satellites [5], provide macroscopic but not microscopic information about the adjustment of the modulation wave to the motion of pinning defects. NMR techniques like relaxation time and linewidth measurements provide the spectral density of the fluctuations and the distribution of the field gradients; however, they do not directly give specific information about the translational motion of a moving nucleus or modulation wave (e.g., how far it moves in a specific time). Conventional pulsed gradient techniques cannot be used in an incommensurate system because the linewidths are too broad and the sensitivity is too low. Our measurements, however, observe a specific form of the magnetization decay which reflects an irreversible change in the NMR frequency due to the spatial motion of the modulation wave. Careful measurement of the time dependence of this decay allows the determina-

tion of the accumulated phase change due to the motions (i.e., the mean squared displacement of the modulation wave). Furthermore, restricted diffusion involving attractive centers [6] or fixed walls [7] results in effects which change the time dependence of the exponent in the magnetization decay from t^3 to t^2 or t, thereby allowing a determination of the crossover distance from free to restricted diffusion and resulting in effects that are very different than those normally seen in typical NMR experiments.

Our experiments were performed on ^{93}Nb in a single crystal of the insulator barium sodium niobate (BSN), which is incommensurate below approximately 580 K [8]. Barium sodium niobate ($Ba_2NaNb_5O_{15}$) is a special case of a system having a four-component order parameter [8] in which two components are frozen and two are fluctuating. Also, BSN is characterized by nonstoichiometry, which undoubtedly is responsible for a large number of mobile point defects, probably sodium vacancies [9]. These defects should lead to a random pinning of the modulation wave (making it a kind of incommensurate glass), but with continuous readjustment of the position of the modulation wave to the instantaneous position of the mobile defects.

In BSN the Nb nuclei are surrounded by oxygen atoms to which they are covalently bound; thus they cannot diffuse. Hence, any motional effects observed in the NMR studies described here must arise from the motion of the modulation wave. The physical model assumed here is that the rapid motions of sodium vacancies [10] cause microadjustments in the modulation wave (due to pinning and depinning). The resulting slow variation in the EFG seen by the static quadrupolar nucleus ^{93}Nb should be equivalent to that experienced by a mobile quadrupolar nucleus diffusing across a spatially varying EFG. Accordingly, we will first consider the behavior of a quadrupolar spin diffusing across a static inhomogeneous EFG arising from a static, pinned modulation wave.

Bloch's equations describing the behavior of the magnetization for a spin diffusing across a magnetic field gradient are given by [11]

$$\frac{\partial \mathbf{M}}{\partial t} = (\mathbf{M} \times \gamma \mathbf{H}) - \frac{M\mathbf{i} + M_y\mathbf{j}}{T_2} - \frac{(M_z - M_0)\mathbf{k}}{T_1} + D\nabla^2\mathbf{M}. \quad (1)$$

For the case of a quadrupolar nucleus diffusing across the inhomogeneous electric field gradients arising from a pinned modulation wave, the frequency $\gamma\mathbf{H}$ (assumed to be in the z direction) in Eq. (1) is replaced by $\gamma\mathbf{H} = [\omega_0 + \Delta\omega(\mathbf{r})]\mathbf{k}$, where ω_0 represents the sum of the static spatially homogeneous Zeeman and quadrupolar interactions in the absence of incommensurability and $\Delta\omega(\mathbf{r})$ represents the change in the NMR frequency arising from the space-dependent electric field gradients of the incommensurate modulation wave at position $\mathbf{r}$.

The NMR (or NQR) angular frequency of a spin at $\mathbf{r}$ due to an incommensurate modulation wave can be related to its position by [12]

$$\omega(\mathbf{r}) = \omega_0 + \omega_1 \cos[\varphi(\mathbf{r})] + \omega_2 \cos^2[\varphi(\mathbf{r})] + \omega_3 \cos^3[\varphi(\mathbf{r})] + \cdots, \quad (2)$$

where $\varphi(\mathbf{r})$ is the phase of the modulation wave at $\mathbf{r}$, and ω_j is proportional to the jth power of the amplitude of the modulation wave. In the plane wave approximation, which is normally valid in the high temperature portion of an incommensurate phase [12], the phase $\varphi(\mathbf{r})$ is equal to $\mathbf{q}\cdot\mathbf{r}$, where $\mathbf{q}$ is the modulation wave vector.

We consider first the simplest case, where only the linear term in Eq. (2) (proportional to ω_1) is kept and the plane wave approximation is assumed. If the time variation of the phase $\varphi(\mathbf{r})$ is sufficiently slow that it can be treated as independent of time for the time duration of a single EFG fluctuation (this is called the "effective local gradient" approximation [13] and is equivalent to replacing the phase and thus the EFG by its average value), the Hahn T_2 decay will be characterized by an exponential dependence on the cube of time t [11], as in the usual case of diffusion along a static linear magnetic field gradient [2]. However, the coefficient will be characteristic of the modulation wave. The dependence of the magnetization on frequency ω can be obtained by replacing $\cos(\mathbf{q}\cdot\mathbf{r})$ by $(\omega - \omega_0)/\omega_1$. We then get

$$M_H(t,\omega) = M(0,\omega)\exp(-t/T_2) \times \exp\{-D\omega_1^2 q^2[1 - (\omega - \omega_0)^2/\omega_1^2]t^3/12\}, \quad (3)$$

where D is the diffusion constant, $M_H(t,\omega)$ is the magnetization in the Hahn decay at time t for those spins whose resonance frequency is ω, and $M(0,\omega)$ is the magnetization at $t = 0$. The ω_1^2 factor, which reflects the magnitude of the EFG tensor variation over the incommensurate modulation wavelength, can be determined from the NMR lineshape and q is known from x-ray and neutron scattering measurements. For a Carr-Purcell (CP) sequence [14], the result is again similar to the usual result, and is given by

$$M_{CP}(t,\omega) = M(0,\omega)\exp(-t/T_2) \times \exp\{-D\omega_1^2 q^2[1 - (\omega - \omega_0)^2/\omega_1^2]\tau^2 t/3\}, \quad (4)$$

where 2τ is the spacing between 180° pulses. Since the CP decay's exponent is linear in t, whereas the Hahn decay's exponent $\propto t^3$, the Hahn decay will be more rapid than the CP decay when sufficient diffusion across large gradients occurs. For both the Hahn and CP sequences, the effective diffusion constant, which is proportional to $D[1 - (\omega - \omega_0)^2/\omega_1^2]$, varies over the inhomogeneously broadened NMR line, having a maximum value in the

center of the line where phasons dominate and going to zero at the edges where amplitudons dominate.

In general, the NMR (or NQR) resonance line for an incommensurate system is inhomogeneously broadened. In order to obtain the decay for the entire line, it is necessary to integrate the decay for the individual spins [obtained from Eq. (3) or (4)] over the inhomogeneous distribution, which is characterized by two edge singularities [12,15] for the linear case considered here.

These results can easily be extended to the case where $\omega(\mathbf{r})$ is a general function, given by $\omega(\mathbf{r}) = \omega_0 + f(\cos\varphi(\mathbf{r}))$ and the phase may have a nonlinear dependence on position $\mathbf{r}$ as in the multisoliton region. Again using the effective local gradient approximation and assuming a one-dimensional modulation wave, the Hahn decay $M_H(t,x)$ for a single spin at position x can be expressed as

$$M_H(t,x) = M(0,x)\exp(-t/T_2) \times \exp[-Df'^2 \sin^2\varphi(x)\,(d\varphi/dx)^2 t^3/12], \tag{5}$$

where f' is the first derivative of f with respect to $\cos\varphi(x)$. Quadratic and higher order terms in the expansion of Eq. (2) can easily be obtained by substitution into the above equation. As in Eqs. (3)–(4), the x dependence of Eq. (5) can be replaced by the dependence on the Larmor angular frequency ω, but the precise mathematical form depends on f and on the dependence of the phase $\varphi(x)$ on x. It is clear from Eq. (5) that the Hahn magnetization will decay with an exponential dependence on t^3, regardless of the precise forms assumed for $f(\cos\varphi)$ or $d\varphi/dx$, provided the effective local gradient approximation is valid, which should be the case for the extremely small displacements corresponding to the modulation wave motion. Nevertheless, the coefficient of t^3 will depend on the nature of the modulation wave, and will be different for restricted diffusion than for the free diffusion, assumed in Eqs. (3)–(5). Also, for very long times the breakdown of the effective gradient approximation can cause departures from the t^3 dependence [13].

We measured both the Hahn decay and the CP decay at 8.5 T over the temperature range 300–650 K for the central transition of ^{93}Nb in a single crystal of BSN. At all temperatures the Hahn decay was more rapid than CP, suggesting that diffusion of the modulation wave is occurring, since the covalently bonded Nb atoms can not diffuse. Recently published T_1 and T_2 ^{93}Nb data [16] are consistent with diffusive motions dominating the relaxation. The CP decay is multiexponential and can be fit by two or more components [17]. This behavior is consistent with the discussion following Eqs. (3) and (4) pointing out that the effective diffusion constant will be different for different portions of the inhomogeneously broadened NMR line.

Figure 1 shows the Hahn decay at $T = 25\,^{\circ}$C obtained with a selective pulse sequence ($H_1 = 8$ G) that excites

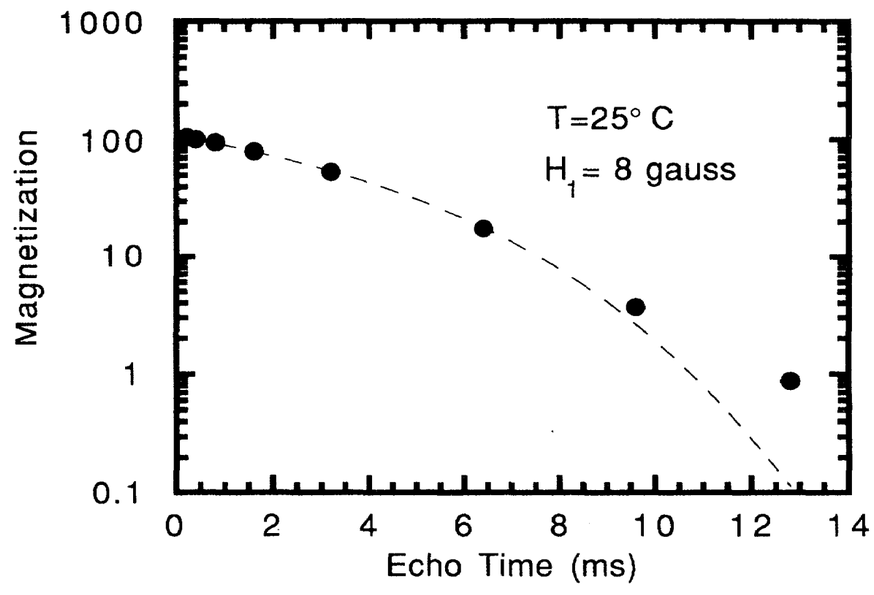

FIG. 1. Magnetization vs echo time in Hahn decay for a selective pulse sequence. The dashed curve represents a fit using Eq. (3), which assumes an exponential dependence of the magnetization on the cube of the echo time, after the dependence on T_2 is removed.

only the central portion of the line. This figure shows that the decay can be fit by a time constant proportional to t^3, as predicted by the above discussion. The fact that the t^3 fit to the decay may not be as good at very long times suggests that restricted diffusion may be important. As we discussed earlier, diffusion near an attractive force center will result in a slower magnetization decay, more likely characterized by a coefficient proportional to t^2. Such behavior would be expected for the signals from Nb nuclei that are located near pinning centers. Another possibility is that this departure from t^3 behavior may be due to motions of sufficiently large range and that the use of an effective local gradient is no longer valid. The time dependence of the magnetization decay has also been studied in other incommensurate systems [18,19] at lower temperatures where the modulation wave is pinned by impurities, and no t^3 dependence was observed.

Figure 2 shows a plot of the temperature dependence of the effective diffusion coefficient D determined from the experimentally measured coefficient of t^3 in the Hahn decay using Eq. (3), using relatively nonselective pulses for which H_1 was 69 G. These data were obtained from the short-time portion of the decay, before the crossover to restricted diffusion. According to Eq. (3) the coefficient of t^3 is $D\omega_1^2 q^2/12$ at the center of the resonance line (where $\omega = \omega_0$). The y axis of this figure was obtained by using $2\pi(20\text{ kHz})$ for ω_1 (determined from NMR linewidth measurements [16] in BSN) and 4.5×10^6 cm^{-1} for the incommensurate wave vector q (determined from x-ray data [8,20]). This behavior shows a significant decrease in effective diffusion constant with decreasing temperature, consistent with the idea that the modulation wave becomes more strongly pinned as the temperature is lowered. The root mean square atomic displacement can be estimated from $\langle x^2\rangle = 2Dt$. For $t = 10$ ms and $D = 10^{-13}$ cm^2/s, the rms displacement is about 4.5 Å, which is consistent with the idea that we

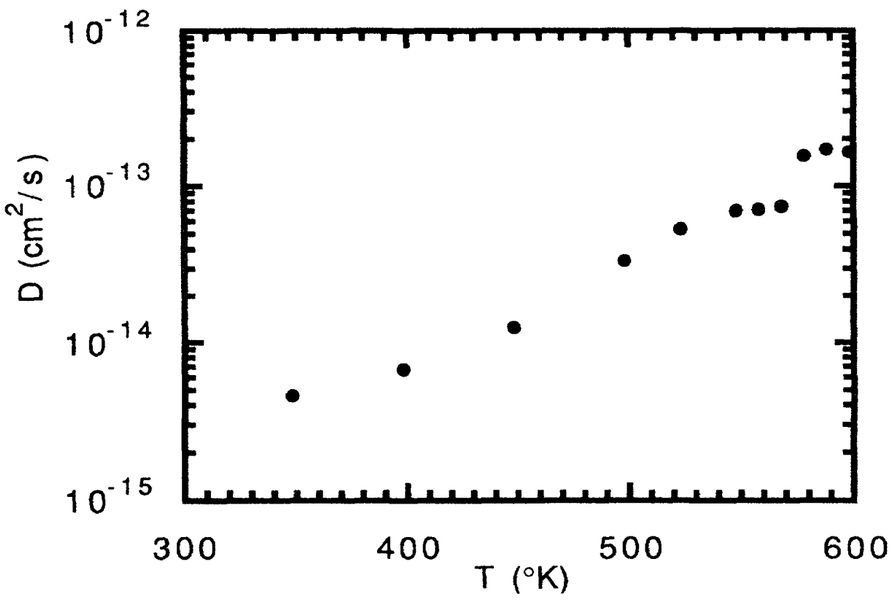

FIG. 2. Diffusion constant D vs temperature. For each point D was determined from the experimentally measured coefficient of t^3 in an exponential fit to the initial part of the Hahn decay before the crossover to restricted diffusion.

are measuring very small amplitude microreadjustments of the modulation wave. These displacements are several orders of magnitude smaller than the smallest observable with conventional magnetic field gradient NMR.

In summary, we have used the principles underlying NMR diffusion techniques to develop a new approach to study electric field gradient fluctuations at the site of stationary quadrupolar nuclei. Instead of using NMR to observe the diffusion of nuclei in large magnetic field gradients, we have used high field NQR to observe the small amplitude fluctuations in the electric field gradient due to diffusive motions of the modulation wave in an incommensurate insulator. This approach has resulted in a much higher sensitivity to very small diffusion constants, corresponding to much smaller atomic displacements, than can be observed by conventional magnetic field gradient NMR. These measurements also give insight into the nature of modulation wave dynamics in incommensurate systems.

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