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Detection of slow modulation wave diffusion in incommensurate barium sodium niobate by ^{93}Nb two-dimensional exchange NMR

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^{93}Nb two-dimensional (2D) exchange NMR was used to study ultraslow motions in incommensurate barium sodium niobate (BSN) in the temperature range 500–560 K. These 2D exchange data provide strong evidence for diffusionlike motion of the modulation wave in BSN. Such motions in BSN had been previously detected by using a complementary NMR experiment, the Hahn spin-echo decay. However, since the Hahn spin-echo decay technique cannot always distinguish unambiguously between different motional mechanisms, this 2D experiment provides definitive confirmation of modulation wave diffusion and rules out other possible motional mechanisms for the Hahn spin-echo decay in this system.

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Considerable attention has been devoted in recent years to understanding the properties of incommensurate (I) systems.[1] These systems have at least two competing periodicities (that of the incommensurate modulation wave (or waves) and that of the underlying crystal structure) whose wave vectors are not rational multiples of one another. Incommensurates exhibit long-range order but no translational symmetry and thus can be regarded as intermediate between perfect crystals and glasses.

Barium sodium niobate $[\mathrm{Ba_2NaNb_5O_{15}}]$ (referred to as BSN) is a special type of I system. The order parameter for the transition from the normal ferroelectric (N) phase to the I phase at $T_I \cong 580\,\mathrm{K}$ has four components in which two components are frozen and two are fluctuating.[2] Another way in which BSN is different from other I systems is that the commensurate phase below $T_c \cong 540\,\mathrm{K}$ exhibits residual incommensurability[3] down to 15 K, and therefore is designated as quasicommensurate (QC). Also BSN is characterized by nonstoichiometry, which is probably related to the presence of a large number of mobile point defects, such as sodium vacancies.[4] These defects randomly pin the modulation wave, which continuously readjusts its position to the instantaneous position of the mobile defects. This random pinning of the modulation wave produces Gaussian line broadening of the ^{93}Nb NMR line shape,[5] resulting in an observed line shape that does not exhibit the characteristic features of the line shapes of other $1q$- or $2q$-modulated I systems.

The existence of ultraslow modulation wave motion in BSN has recently been inferred from ^{93}Nb Hahn spin-echo quadrupole perturbed NMR measurements.[6] Since Nb nuclei are surrounded by oxygen atoms to which they are covalently bound, they cannot move. The explanation for the more rapid Hahn spin-echo decay versus the Carr-Purcell-Meiboom-Gill (CPMG) decay was that the modulation wave moves, resulting in a time-dependent electric-field gradient (EFG) seen by the Nb nuclei. However, a short Hahn spin-echo decay[7–9] can, in some systems, be due to several possible motional mechanisms,[9–11] which cannot be easily distinguished just by observation of a more rapid Hahn echo decay.

In this paper we present ^{93}Nb two-dimensional (2D) exchange NMR data which provide strong evidence for the existence of progressive motion of the modulation wave, thereby confirming that the rapid Hahn echo decay earlier observed in the incommensurate phase of BSN is indeed due to modulation wave diffusion.

In a 2D exchange NMR experiment[12] the nuclear resonance frequencies are measured coherently at the beginning and at the end of the mixing period t_{mix}. The hopping of a nucleus from one lattice site to another produces a change in its local environment and consequently a change of the resonance frequency. A similar effect occurs if the environment of the resonant nucleus is changed due to motions of the surrounding atoms. The static nuclei with unchanged resonance frequencies contribute to the diagonal ($|f_1|=|f_2|$) of the 2D spectrum. The nuclei which during t_{mix} jump to other lattice sites (or experience a change in the environment due to motion of the surrounding atoms) create off-diagonal intensities (called cross peaks, $|f_1|\neq|f_2|$) in the 2D spectrum. For small displacements for which the change in the NMR frequency due to motions is very small compared to the inhomogeneous linewidth (which determines the length of the diagonal in the 2D spectrum), the contour of a 2D spectrum has a diagonal shape with cross peaks that are unresolved from the continuous diagonal. The width of the diagonal increases with t_{mix} until it reaches saturation for restricted spatial motion.

Our ^{93}Nb 2D exchange NMR experiments were performed in a single crystal of BSN for a crystal orientation $B_0 \| c$, in a magnetic field $B_0 = 8.5$ T, at 86.82 MHz, by irradiating the central transition $1/2 \leftrightarrow -1/2$. The pulse sequence is based on the basic four-pulse stimulated echo 2D exchange sequence,[12,13] which consists of three 90° pulses and a 180° pulse at the end. The 180° pulse is used to shift the stimulated echo by an extra time interval in order to avoid ringdown effects. The hypercomplex Fourier transform (FT) procedure[13,14] is used in processing the 2D signal in order to obtain pure absorption 2D spectra with sign discrimination in both frequency dimensions.

The width (normalized to the contour length) of the diagonal, Δf, [Fig. 1(a)] was measured at a fixed position in the 2D spectrum at different mixing times. The actual frequency change Δf_{exch} due to motions was then extracted, using[15]

$$\Delta f^2 = \Delta f^2(t_{\mathrm{mix}}=0) + \Delta f^2_{\mathrm{exch}}, \tag{1}$$

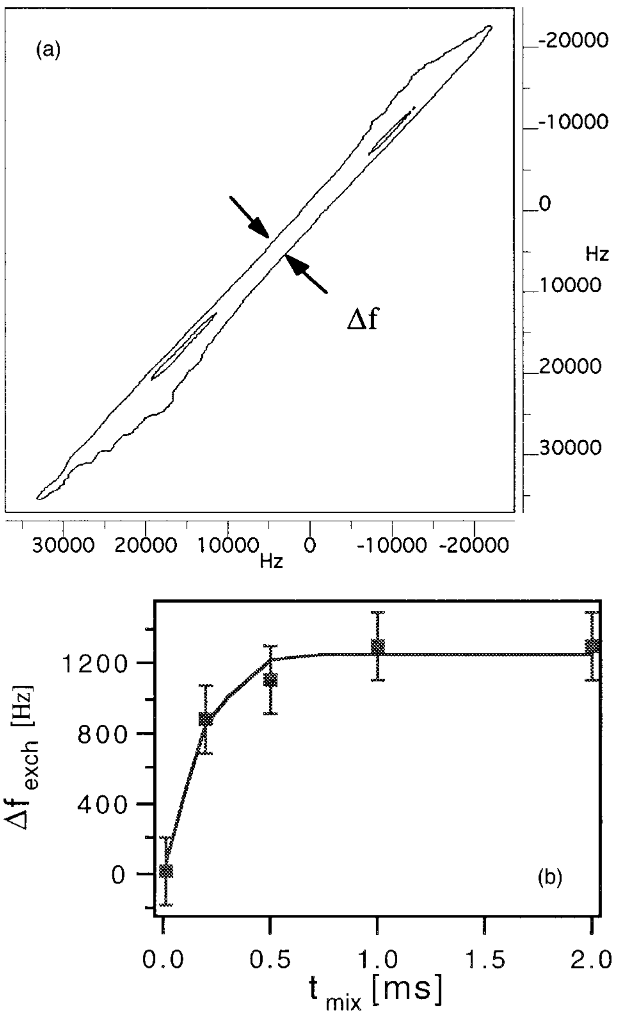

FIG. 1. (a) ^{93}Nb 2D exchange NMR spectrum for $t_{\rm mix}=10\ \mu$s, at 560 K. (b) The variation with mixing time $t_{\rm mix}$ at 560 K of the frequency shift $\Delta f_{\rm exch}$ due to motions. The solid line is a theoretical fit to Eq. (3).

which is valid for Gaussian line shapes. This formula takes into account that the no-exchange ($t_{\rm mix}=0$) spectrum has a finite width, which for Gaussian line shapes is related[16] to the spin-spin relaxation time T_2 by $\Delta f=3.34/\sqrt{2}\pi T_2$, with Δf measured in Hz.

As the mixing time increases, the frequency change $\Delta f_{\rm exch}$ due to motions progressively increases until it reaches an asymptotic value [Fig. 1(b)], suggesting that the motion is spatially restricted. The modulation wave in structurally *I* systems originates from progressive displacements and/or misorientations of a group of atoms from their equilibrium position. These displacements are limited by the amplitude of the modulation wave. For an ideal *I* system without impurities there is no particular phase of the modulation wave which minimizes the free energy of the system. Consequently, such an ideal system would, in principle, be characterized by a freely sliding modulation wave. However, such motion is not observed in real crystals since impurities randomly pin the wave. The progressive variation of $\Delta f_{\rm exch}$ with $t_{\rm mix}$ suggests that the observed motion is due to the motion of the modulation wave, which typically moves in steps that are small compared to its wavelength.[8,17–19] This situation contrasts to the situation in which an atom jumps between two sites. In this case, the variation of the frequency change with mixing time looks completely different, showing a sudden jump at a given mixing time, from zero to a fixed value. We have observed both of these motional mechanisms, the modulation wave motion and the two-site jump motion, by going from the incommensurate to the paraelectric phase in $\mathrm{Rb_2ZnCl_4}$.[19]

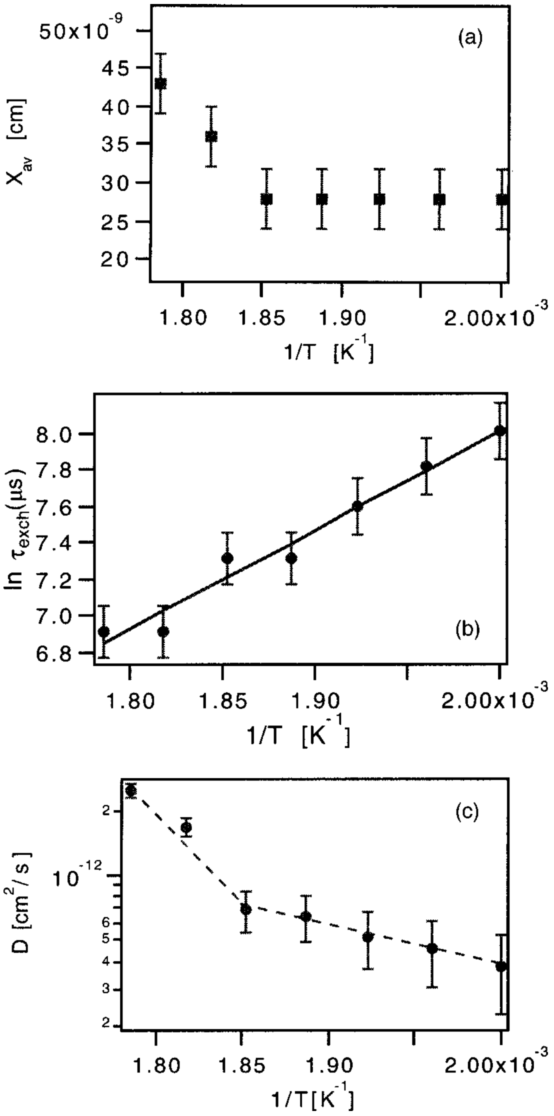

FIG. 2. (a) The variation of the maximum average modulation wave displacement $X_{\rm av}$ with temperature. (b) The variation of the correlation time $\tau_{\rm exch}$ with temperature. The straight line is a fit to the data assuming Arrhenius behavior with an activation energy $E_a=0.47\pm0.05$ eV. (c) The variation of the diffusion coefficient with temperature. The dotted line is a guide for the eye.

We can estimate the average maximum distance $X_{\rm av}$ traveled by the modulation wave by using the frequency-space relation[20] at the center of the inhomogeneously broadened spectrum,

$$\pi\frac{\Delta f_{\rm INC}}{\lambda}=\frac{\Delta f_{\rm exch}}{X_{\rm av}}. \tag{2}$$

Here, Δf_{INC} is the incommensurate splitting of the line shape obtained by fitting the Nb NMR line to a superposition of two Gaussian lines,[5] and λ is the wavelength of the I modulation wave ($\lambda = 1.4 \times 10^{-6}$ cm from Ref. 2). Using Eq. (2) we determined that the average maximum displacement X_{av} of the modulation wave is approximately 2.8 ± 0.4 Å in the quasicommensurate phase (in a temperature range 500–540 K). This displacement increases at higher temperatures in the I region, being 3.6 ± 0.4 Å at 550 K and 4.3 ± 0.4 Å at 560 K. Figure 2(a) is a plot of the temperature dependence of X_{av} over the QI and I phases.

By assuming that the modulation wave moves with equal probability in both directions (since there is no reason for a preferred direction), we can determine the correlation time τ_{exch} of the modulation wave motion by fitting the curve of Fig. 1(b) to the equation[15]

$$\Delta f_{\mathrm{exch}} = A \tanh \frac{t_{\mathrm{mix}}}{\tau_{\mathrm{exch}}}, \tag{3}$$

where A is a fit parameter. Using this equation we determined values for the correlation time ranging between $\tau_{\mathrm{exch}} \cong 3$ ms at 500 K and $\tau_{\mathrm{exch}} \cong 1$ ms at 560 K. As can be seen from Fig. 2(b), within experimental error the temperature dependence of τ_{exch} is Arrhenius and is characterized by a single activation energy (0.47 ± 0.05 eV) in both the I and QI phases. These experiments proved to be extremely time consuming, since one experiment for a single mixing time lasted up to three days.

We estimated the diffusion coefficient for modulation wave diffusive-type motion using the formula $D = X_{\mathrm{av}}^2/2\tau_{\mathrm{exch}}$. The diffusion coefficient D shown in Fig. 2(c) varies in a range between 2.2×10^{-13} cm/s^2 at 500 K and 3.8×10^{-12} cm/s^2 at 560 K. A change in the slope can be seen at the temperature 540 K of the QI-to-I transition. However, as we have seen from Figs. 2(a) and (b), this change represents primarily the temperature dependence of X_{av} in the I phase, rather than different activation energies in the two phases.

The results described above using 2D exchange NMR compare reasonably well with the earlier results (in Ref. 6) using the Hahn spin-echo decay technique. The activation energies are comparable and the absolute values for D agree within a factor of 3. Residual discrepancies in the absolute values of D probably reflect systematic errors arising from differences in the two approaches. Moreover, the equation, $D = X_{\mathrm{av}}^2/2\tau_{\mathrm{exch}}$, which was used to provide an estimate for D from 2D exchange data, is an approximation that is probably not strictly valid for modulation wave diffusion. Other possible systematic errors may be due to experimental errors in determining X_{av} and in correcting for T_2 attenuation in the earlier Hahn-echo experiment.

In summary, our ^{93}Nb 2D exchange NMR data provide strong evidence for the diffusionlike motion of the modulation wave in BSN. Such motion in BSN had been previously inferred from a complementary NMR experiment, the Hahn spin-echo magnetization decay. However, since the Hahn spin-echo experiment cannot unambiguously distinguish between different types of motional mechanisms, this 2D experiment provides definitive confirmation of modulation wave diffusion. We also determined the average displacement of the modulation wave and estimated the correlation time and the diffusion coefficient D. Measurements of the temperature dependence of D show markedly different slopes in the QI and I phases.

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