NMR Study of the Structure and Motion of Charge-Density Waves in $NbSe_3$

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The authors report NMR measurements of the ^{93}Nb resonance in the charge-density-wave (CDW) conductor $NbSe_3$ on aligned, multicrystalline samples. They have observed the resonance with and without current flow in the sample at temperatures above 59 K, where a single incommensurate CDW is present. Results include (1) a demonstration that the CDW is not discommensurate, (2) quantitative measurements of CDW displacements below threshold, and (3) evidence, including current-induced motional narrowing, of CDW motion throughout the entire sample, above the threshold.

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$NbSe_3$ is a material possessing incommensurate charge-density waves (CDW's). One CDW is present between 144 and 59 K, while two coexisting CDW's are observed below 59 K. A number of unusual phenomena are observed in this material, which are thought to be related to the presence of CDW's. These phenomena include non-Ohmic conductivity[1] and narrow-band voltage noise,[2] properties observed in both CDW temperature regimes. In this paper, we present results for the higher-temperature regime, in which only one CDW is present. We show that the CDW is "plane-wave incommensurate," rather than "discommensurate," measure the CDW displacement produced by electric fields below threshold, and prove that the entire CDW is set in motion by electric fields above threshold.

Typical $NbSe_3$ crystals are hairlike fibers, with dimensions $1\times10\times10\,000$ μm^3. To obtain sharp, single-crystal NMR spectra with sufficient intensity, one needs an aligned multicrystalline $NbSe_3$ sample. Even so, extensive signal averaging is required (typically 10^5 echoes). For the first set of experiments, we constructed a sample containing roughly 300 crystals, aligned on all three axes. The second set of experiments required an aligned sample with attached voltage leads, which we constructed with 30 crystals, each 1 cm in length. In this sample we observe $\sim 6\times10^{16}$ nuclei, which typically required the averaging of 10^6 echoes. The crystals, grown in our laboratory, are of high purity, as evidenced by the conductivity thresholds, which are on the order of 100 mV/cm for the upper CDW (minimum value), comparable to the best reported in the literature. One can obtain much larger crystals for the blue-bronze system, but Douglass, Scheemeyer, and Spengler[3] and Berthier[3] have used NMR to look for CDW motion in that system, without observing the effects reported here.

Since ^{93}Nb has a spin of $\frac{9}{2}$, the NMR spectra consist of nine lines split by the electric quadrupole coupling. We report observations of the central line ($m=\frac{1}{2}$ to $m=-\frac{1}{2}$ transition) of the ^{93}Nb NMR spectrum, for each Nb site described below. The resonance positions of these lines are determined by the Knight shift and the second-order quadrupole shift, the latter of which is related to local electric field gradients (EFG's). We separate the two shift contributions through their magnetic field dependences. We have observed line shapes at fields in the range of 25 to 85 kG.

In the normal state ($T > 144$ K), $NbSe_3$ has three types of chains, which Wilson[4] has labeled the "red," "orange," and "yellow." Spectra observed above 144 K clearly show three sets of NMR lines corresponding to the three inequivalent Nb sites. We identify one of these sets with the yellow site through its EFG tensor symmetry. The effect of the high-temperature CDW transition is a broadening of the yellow line (Fig. 1). The red and orange lines are unaffected, demonstrating clearly that the CDW is localized on the yellow chain. This result is consistent with the results of Devreux.[5]

It is convenient to introduce the concepts of plane-wave–incommensurate and discommensurate[6] CDW's. In the former, there is a single wavelength which is incommensurate with the lattice. For the latter, the average wavelength is incommensurate, but locally the CDW has commensurate regions separated by regions of phase slip, called discommensurations. Discommensurate CDW's have been observed in the layer-type CDW materials.[7]

The ability of NMR to distinguish a plane-wave–incommensurate CDW from one possessing a discommensurate structure has been demonstrated previously.[5,7,8] In commensurate regions, NMR lines are discrete, whereas in plane-wave–incommensurate regions, the lines are a broad continuum. In a discommensurate structure the lines are a superposition of the two types.

The key to our analysis of the line shapes is the contrast of the broad yellow line seen in aligned single crystals in the presence of a static field, compared to the narrow line seen earlier in the zero-field study.[9] This result implies that there is a distribution in the

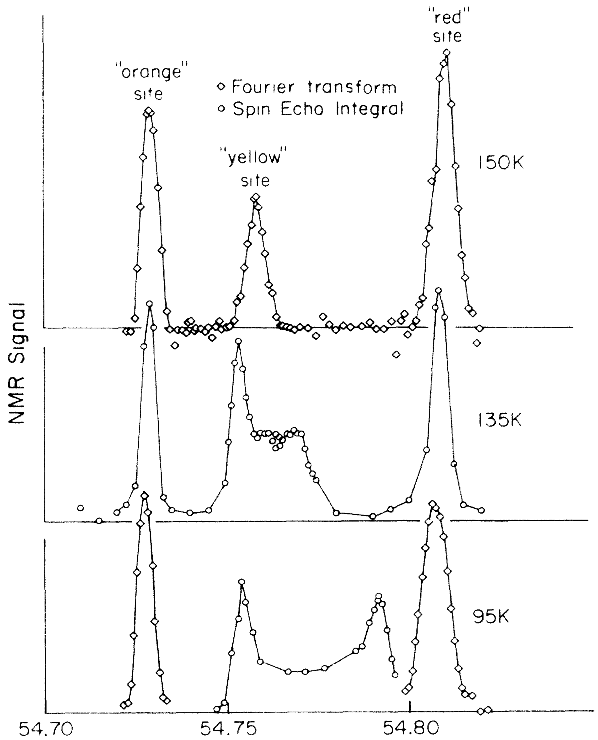

FIG. 1. $NbSe_3$ ^{93}Nb central transitions at 52.478 kG, $H_0 \parallel b$, as a function of temperature. The three inequivalent sites and the CDW broadening of the yellow line are apparent. Data are uncorrected for relaxation times.

orientation of the EFG principal axes, but not the principal values, along the yellow chain, and we can successfully describe our line shapes with such a model, taking principal values from the zero-field study.

The orientation distribution which describes the line shape is a simple modulation,

$$\beta(x)=\beta_0+\Delta\beta\sin[\phi(x)], \quad (1)$$

where β is an orientation angle about a fixed axis, and ϕ is the CDW phase. To describe the full range of possibilities, we assume that the phase satisfies a sine-Gordon equation,

$$d^2\phi/dx^2=\alpha^2\sin(4\phi), \quad (2)$$

where, if the average wave vector $(d\phi/dx)$ is fixed, the parameter α describes any situation from plane-wave incommensurate $(\alpha\to 0)$ to extremely discommensurate $(\alpha\to\infty)$.

We have generated these curves numerically (Fig. 2). The best fit is the plane-wave–incommensurate curve, with even a small amount of discommensuration bringing the calculated curves out of line with the data. The most distortion that we can allow is $\alpha=1.5$ (assuming that the scale of x is chosen so that the

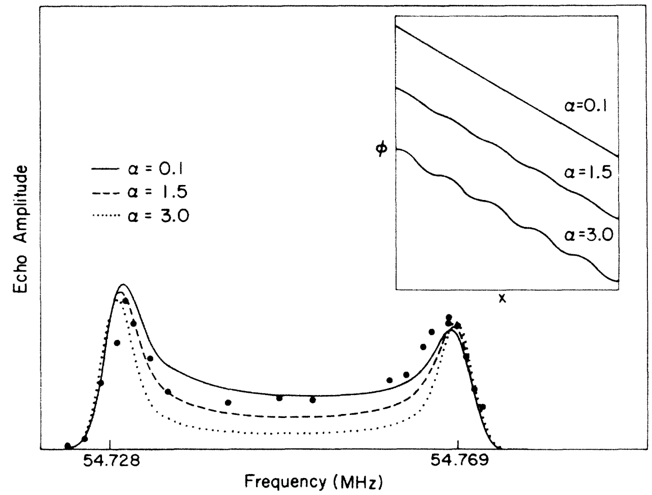

FIG. 2. Yellow line shape at 95 K and 52.478 kG. The theoretical curves follow the description in the text. The associated phase profiles (inset) illustrate the amounts of discommensuration. An even closer fit (not shown) is obtained by the addition of a small amount of the second harmonic (4%) to the EFG modulation.

phase advances an extra $\pi/2$ per unit length), which is essentially a uniform phase distribution. Therefore, we find that discommensurations are not important in $NbSe_3$, from temperatures of 120 to 60 K.

To investigate the voltage response of the CDW, we have observed the NMR while applying currents, using the aligned sample with voltage contacts at a fixed temperature of 77 K (the sample is immersed in liquid nitrogen), oriented with H_0 along b, the conduction axis. The sample conduction threshold at 77 K is 200 mV/cm, although the shape of the threshold at this temperature is not as sharp as at some temperatures.

The first experiment is an investigation of pulsed current below the threshold. We demonstrate and quantitatively measure the induced CDW displacement, the likely source of the anomalously large dielectric constant observed in $NbSe_3$.[10] The principle of these measurements is that when the CDW is displaced, the precession frequency of every nucleus changes, the amount depending on the size of the displacement and on where the nucleus sits in the CDW. We measured the frequency shift with the use of spin echoes to observe the NMR, but we added a dc voltage pulse between the 90° and 180° rf pulses (Fig. 3, inset). In some cases we added a second, identical dc voltage pulse following the 180° rf pulse. This sequence was repeated many times in succession for signal averaging. The dc voltage pulses were unidirectional.

The results are fitted with a model in which the CDW is displaced by the voltage pulse, and then rapidly relaxes to its original position once the pulse is turned off. The expected echo shape can be computed

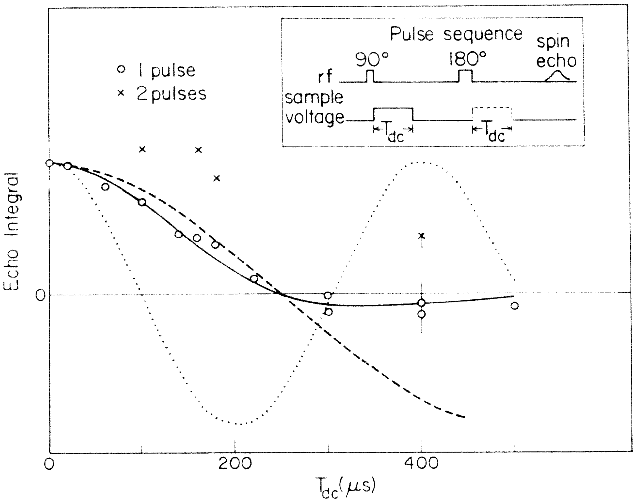

FIG. 3. Data from the CDW-displacement experiment and (inset) the pulse sequence. Theoretical curves are from the echo-simulation calculations described in the text, using phase displacements of 5° with no distribution (dotted line), 2° with no distribution (dashed line), and 2° with a Gaussian distribution of full width 4° (solid line). The error bars on the data are representative.

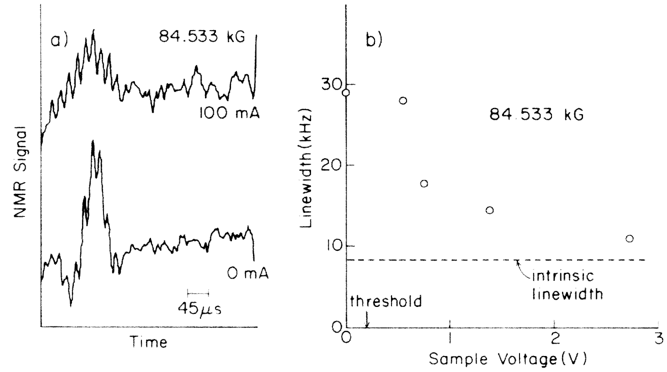

FIG. 4. (a) Spin echoes at 77 K illustrating the current-driven motional narrowing of the yellow line. The broader echo implies a narrower line. The superimposed oscillations are the nearby resonance of the red site. (b) Bias-dependence of the motional narrowing as measured from the echo breadth. The intrinsic is that of the red and orange sites.

by use of our theory of the line shape, provided that one knows the CDW phase displacement produced by the dc voltage pulse. If the phase displacement were the same at all nuclei, the echo integral would vary sinusoidally with the pulse length, in the single-pulse experiment. If, however, the CDW phase displacement is distributed, the echo integral will consist of a dying oscillation. We do observe such a dying oscillation in the integral, for a dc bias about $\frac{3}{4}$ of the threshold value (Fig. 3). With a second identical pulse applied after the 180° rf pulse, though, the echo reforms much better. This shows that the second pulse produces the same NMR frequency shifts as the first, demonstrating that the CDW displacements are reproducible.

The theoretical curves (Fig. 3) were generated with a numerical echo-simulation routine, which used the line-shape fit (outlined above), with a uniformly incommensurate phase profile, and assumed that the CDW phase is displaced while the voltage pulse is on. The only adjustable parameters are the phase displacement and its distribution. The curve which fits best is associated with an average displacement of 2° and a wide distribution of displacements. The average displacement is much smaller than expected from a rigid classical model with a uniform barrier height (about 50° at this voltage). This result could follow from tunneling,[11] although disorder in the CDW[12] may also produce the same qualitative result. Indeed, the distribution of observed displacements may also indicate the importance of disorder.

In observations of the CDW above the threshold, we find two important results. The first is the motional narrowing of the CDW line, and the second is its dynamic saturation.

The motional narrowing provides a demonstration that the CDW is in bulk motion above the conduction threshold. We see the yellow line, broadened by the stationary CDW, collapse to a narrow line of the same amplitude during dc current flow. Figure 4(a) shows the spin echo obtained with and without dc current. Since the spin echo is related to the linewidth through its Fourier transform, the duration of the echo can be used to measure the linewidth. The broader echo with dc current implies a narrower line when current flows.

The limiting value of the narrowed linewidth at high current [Fig. 4(b)] is equal to the linewidths of the two non-CDW sites, which arise from strains or other intrinsic crystal inhomogeneities. Thus the static CDW broadening is completely removed by the dc current. This imples that each nucleus rapidly samples the entire range of charge density. It has been well established from x-ray studies[13] that large currents do not affect the CDW amplitude, which rules out the disappearance of the CDW as an alternative explanation for the data.

In NMR experiments,[14] motional narrowing occurs when the motion frequency exceeds the linewidth (in this case 30 kHz). Our experiment yields significant narrowing at a voltage of somewhat less than 3 times the threshold. We can estimate the sliding frequency at this voltage, assuming a uniformly sliding CDW. One has, $\nu_{CDW} = I_{CDW}/Ane\lambda$. We estimate A (the sample cross section) from electron-microscope studies to be 1370 μm^2. I_{CDW}, the non-Ohmic excess current, we measure directly. Also, $n = 1.9 \times 10^{21}$ cm^{-3}, assuming $0.5e$ per yellow Nb, and $\lambda = 14$ Å is the CDW wavelength. This yields $\nu_{CDW} = 1.4$ MHz, somewhat larger than the frequency required for narrowing. This implies that large portions of the CDW are moving slower than the average rate. This is consistent with the picture advanced by Fisher,[15] although it may simply represent a threshold distribution in our crystals, an effect which may be particularly important at 77 K, where the threshold is not as sharp as at higher temperatures.

The saturation of the nuclear magnetization is an observation which provides an additional measure of the local motion spectrum of the CDW. We applied dc current to the sample, allowing the spins to equilibrate, then turned off the current, and observed the spin echo. The observed reduction of the spin-echo amplitude implies that transitions are being induced between nuclear Zeeman levels, reducing the population difference from its thermal-equilibrium value. This effect requires that components of the CDW motion spectrum reach the NMR frequency (88 MHz). The mechanism is quadrupole couplings to fluctuating EFG's, and the situation is akin to nuclear acoustic resonance,[16] in which fluctuations are driven externally by ultrasound. In our case, the source of fluctuations is the sliding CDW.

The saturation onset is at 0.95–1.05 V/cm, and the magnetization is reduced by as much as 75%. At the onset bias the fundamental sliding frequency (estimated as before) is roughly 8 MHz. Though this is somewhat less than the frequency required for saturation, on the order of ten harmonics are often observed in the narrow-band noise spectrum,[2] and our observations are consistent with such a motion spectrum affecting the typical nucleus. In addition, the amount of echo reduction implies that the bulk of the sample experiences such a fluctuation spectrum.

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