Excitations in Incommensurate Biphenyl: Proton Spin-Lattice Relaxation

Shang-Bin Liu and Mark S. Conradi

Department of Physics, College of William and Mary, Williamsburg, Virginia 23185

In the upper incommensurate phase of biphenyl, spin relaxation is relatively rapid, because of low-frequency excitations (phasons). The relaxation follows $T_1^{-1} \sim T^{4/3}\omega^{-1/3}$; this is the first report of a Larmor-frequency dependence of T_1 in an incommensurately distorted solid. The frequency dependence suggests that the phasons are gapless. In the low-temperature incommensurate phase, peaks in T_1^{-1} are evident at low frequencies. The motion responsible is thermally activated and may kinetically inhibit commensuration.

Incommensurately distorted solids are predicted to have excitations of the distortion wave, both in amplitude and phase.[1] The phase excitations (phasons) in a pure material should be gapless ($\omega \rightarrow 0$ as $k \rightarrow 0$), because of the independence of the total free energy on the initial phase of the distortion. However, impurities and defects may pin the distortion wave, introducing a gap in the phason spectrum. Also, discrete lattice effects[2] may intrinsically pin the wave and create a phason gap; in this case the solid is not truly incommensurate. In any event, the low-frequency phase excitations should dominate spin-lattice relaxation in incommensurate insulators. Indeed, Blinc and coworkers have found this to be true in a number of incommensurate solids.[3] However, no dependence of T_1 on the Larmor frequency has been observed and the incommensurate phases studied do not exist over wide temperature intervals. Hence it cannot be determined whether the spin relaxation is via direct or Raman processes, nor whether the phasons are indeed gapless.

We report here proton spin-lattice relaxation measurements on biphenyl from 300 to 4 K and at frequencies from 9 kHz to 58.5 MHz. Power-law temperature and frequency dependences are observed, as well as additional relaxation peaks due to a thermally activated motion.

Biphenyl ($C_{12}H_{10}$) above 40.4 K has a monoclinic $P2_1/a$ ($z = 2$) crystal structure; each molecule has its two phenyl groups coplanar in this "normal" phase (I).[4] Below 40.4 K ($T_{I,II}$), the two rings twist in opposite senses as a result of a combination of intramolecular and intermolecular forces.[5] The distortion (twist angle) of the unit cells oscillates through space with an incommensurate wave vector in this phase (II): $q^* = \pm\delta_a\hat{a} \pm \frac{1}{2}(1-\delta_b)\hat{b}$.[6] The distortion is nearly sinusoidal in II, since higher-order diffraction satellites (involving harmonics of the distortion wave vector) are not observed.[7] At 16.8 K ($T_{II,III}$) a partial lock-in transition occurs, with δ_a going to zero but δ_b staying incommensurate. Phase III is believed to presist to the lowest temperatures, since biphenyl remains incommensurate down to 1.6 K.[7] The lack of a commensu-

rate ground state is a remarkable and unusual feature of biphenyl's distortion.

The measurements reported here were performed on a single crystal of biphenyl grown from the melt. The crystal orientation, though not determined, was held constant through the measurements. At 5.0, 21.3, and 58.5 MHz a standard pulse sequence was used to determine T_1: saturate—wait—inspect. Because the T_1 values are long, it was possible to employ field cycling to measure T_1 at 0.38 MHz (obtained in the residual field of our electromagnet). The spins were first magnetized at 21.3 MHz, the magnet current was decreased to zero, and the spins were allowed to relax for a variable time in the low field. The magnet was reenergized to 21.3 MHz, the field was stabilized again, and then the magnetization was inspected. Care was taken to ensure that the field changes always took the same amount of time, so that relaxation during these changes did not enter the measured T_1 values. The lowest-frequency data are measurements of relaxation in the dipolar ordered state (T_{1D}).[8] The Jeener-Broekaert pulse sequence[9] (90_x-t-45_y-T-45) was used. The T_{1D} values so determined are treated as T_1 values at the low frequency of 9 kHz. This value of ν_{local} is obtained from the theory of spin temperature in the rotating frame[8]:

$$(2\pi\nu_{local})^2 = M_2/3,$$

with M_2 the second moment of the resonance line shape. The value of M_2, 8.4×10^9 rad^2/s^2, was determined with magic echoes,[10] a scheme that essentially displaces the origin of the free-induction decay away from the receiver blocking. Because the dipole interactions are modulated only slightly by the lattice distortion, the linewidth and M_2 are essentially independent of temperature. Because of the dipole interactions, the spins form a thermodynamic system.[8] Thus, unlike previous reports in inhomogeneously broadened systems,[3,11] there can be no variation of T_1 across the resonance line.

The relaxation data appear in Fig. 1. Well above $T_{I,II}$ (i.e., 60 to 150 K) the relaxation rate T_1^{-1} is very small, as expected for a rigid solid with few low-
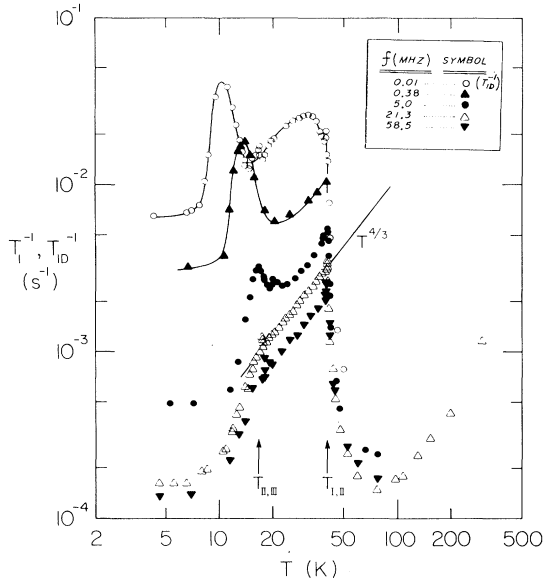
FIG. 1. The spin-lattice relaxation rates T_1^{-1} and T_{1D}^{-1} for biphenyl. The transitions from normal to incommensurate at 40.4 K ($T_{I,II}$) and incommensurate to incommensurate at 16.8 K ($T_{II,III}$) are shown. Temperature scale is logarithmic.

FIG. 2. Critical dependence of T_1 at 21.3 MHz as the normal-incommensurate transition at 40.4 K is approached from above. Data at the other frequencies behave similarly.

frequency excitations (only acoustic phonons). The long T_1 values indicate that the sample has few paramagnetic impurities. The relaxation increases near room temperature, as studied previously.[12]

As the I-II phase transition at 40.4 K is approached from above, the relaxation rate rises dramatically, as a result of critical slowing of the fluctuations.[13] Presumably, these fluctuations involve small regions of the sample that briefly take on the incommensurate structure. As $T \rightarrow T_{I,II}^+$, the spatial and temporal durations of the fluctuations are expected to increase critically.

As shown in Fig. 2, the data are fitted by $T_1 \sim (T - T_{I,II})^{1.05}$ in an interval from 1 to 15 K above $T_{I,II}$ (taken as 40.4 K). The power-law behavior is not expected to hold too near $T_{I,II}$ where the fast-motion limit (all fluctuations faster than the resonance frequency) breaks down.[13] This breakdown produces the frequency dependence seen just above $T_{I,II}$ in Fig. 1. Well above $T_{I,II}$ the power-law behavior is expected not to hold for two reasons: The usual finite extent of the region where critical scaling holds and the background T_1^{-1} which, though small, obscures the critical relaxation well away from $T_{I,II}$. It is interesting that a similar exponent describes the critical spin relaxation in paraterphenyl,[14] which undergoes a similar phase transition to a commensurate structure at 193 K.[5]

The spin relaxation in the incommensurate phase II is considerably more rapid than in the bulk of phase I. This shows the dominant role in spin relaxation performed by the low-frequency excitations which are *unique* to this phase: phasons. The data at 21.3 and
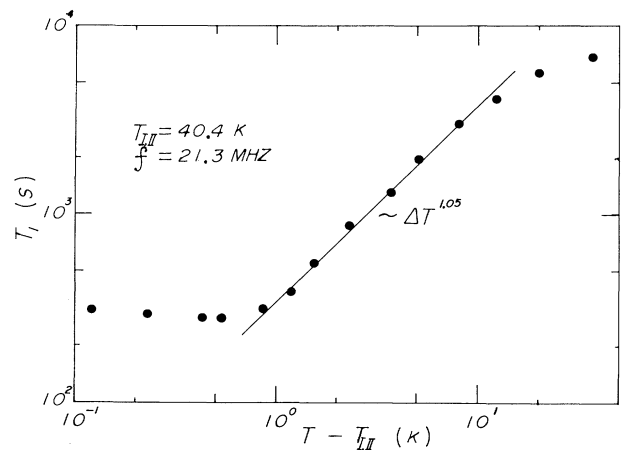
58.5 MHz have parallel temperature dependences, being well described by $T^{4/3}$ as indicated by the solid line in Fig. 1. The value of the exponent should not be affected much by the presence of background relaxation, since the relaxation in phase II is more than ten times faster than the background relaxation.

The frequency dependence of T_1^{-1} at two temperatures in phase II is displayed in Fig. 3, with the solid lines corresponding to $T_1^{-1} \sim \omega^{-0.32}$. The fit is good, even if the T_{1D}^{-1} data at 9 kHz are included. Thus the power-law frequency dependence extends over at least three and one-half decades. This is the first report of frequency-dependent spin relaxation in an incommensurately distorted solid (variation of T_1 across inhomogeneously broadened lines has been reported,[3,11] but never a Larmor-frequency dependence). The increase in relaxation at low frequencies indicates that some of the fluctuations are slower than resonance fre-
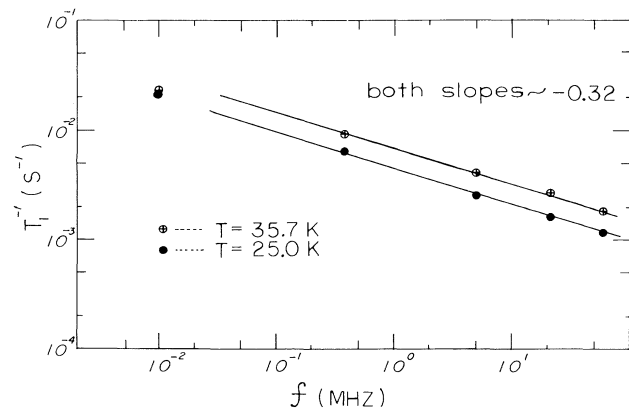

FIG. 3. The frequency dependence of T_1^{-1} of biphenyl at two temperatures in the upper incommensurate phase (II).

quencies. This suggests that the phasons in phase II are indeed gapless, since the measurements here extend to very low frequencies. Also, the observed frequency dependence of T_1 confirms that phasons are responsible for the enhanced relaxation in phase II: Away from the I-II transition, amplitudon frequencies are expected to be much larger ($\sim 10^{11}$ s^{-1}) than spin frequencies, producing frequency-independent relaxation from amplitudons.

Power-law frequency and temperature dependences are common results for spin relaxation via acoustic phonons.[15-17] Hence, it is appropriate to calculate here the relaxation expected from phasons. Acoustic phonons and phasons share the property that they are gapless, or nearly so. Although acoustic phonons are strictly gapless because of translational invariance of the interactions, the phason spectrum may have a small gap, as mentioned above. Nevertheless, we assume in what follows that $\omega \sim |k|$ for both acoustic phonons and phasons.

The frequency dependence of the relaxation in biphenyl indicates that Raman processes are not involved. In a Raman process[15-17] one lattice excitation is destroyed and another is created, the energy difference being equal to the change in spin Zeeman energy. The entire excitation spectrum is effective in a Raman process, not just those excitations resonant with the spins. Since the excitation spectrum extends to $\sim 10^{12}$ s^{-1}, spin frequencies are negligible. Thus, no Larmor-frequency dependence of Raman relaxation is expected. Hence, we calculate the relaxation due to direct absorption or emission of a resonant phonon or phason by a nuclear spin. With acoustic phonons, spins couple to the *relative displacements* of the lattice (i.e., the gradient of displacement)[15-17]; this is true for modulation of the dipolar spin interactions (such as in $C_{12}H_{10}$) as well as for quadrupolar relaxation by time-dependent electric field gradients. In the long-wavelength limit and at high temperatures ($kT \gg \hbar\omega$), this yields $T_1^{-1} \sim n(\omega) T$, where $n(\omega)$ is the phonon density of modes at the resonance frequency ω. In three dimensions one has $n(\omega) \sim \omega^2$, yielding $T_1^{-1} \sim \omega^2 T^1$, a well-known result. By way of comparison, with phasons spins couple *directly* to the resulting lattice displacements. This occurs because phasons are *optical* distortions of the high-temperature structure. Indeed, this is the unique aspect of spin relaxation via phasons: Phasons are essentially gapless yet optical. Hence, for relaxation by phasons, one has $T_1^{-1} \sim n(\omega) T\omega^{-2}$, where ω^{-2} is the factor relating atomic displacements and phason frequency. In three dimensions this becomes $T_1^{-1} \sim \omega^0 T^1$. This may be compared to the experimental result reported here, $T_1^{-1} \sim \omega^{-1/3} T^{4/3}$. Clearly, both the frequency and temperature exponents predicted above differ by $\pm \frac{1}{3}$ from the experimental values. We remark that the ex-

ponents obtained above do not require an isotropic phason spectrum, but are general results when ω and k are linearly related for small ω.

Zumer and Blinc have calculated T_1^{-1} for the direct phason process.[18] They include a damping parameter Γ on all the phason modes, independent of frequency. Although they do not explicitly calculate the undamped, gapless case their equations yield $T_1^{-1} \sim \omega^0 T^1$ for $\Gamma = 0$, in agreement with the simple arguments above. In the limit that $\Gamma \gg \omega$ and assuming a nearly gapless spectrum [$\omega_{gap} \ll (\Gamma\omega)^{1/2}$], they find that $T_1^{-1} \sim \omega^{-1/2} T^1$. This prediction, too, does not agree with the experimental findings. We note that any direct process will lead to $T_1^{-1} \sim T$, unless the excitation spectrum itself or the damping parameter is temperature dependent.

Pronounced peaks in the spin relaxation at low frequencies and low temperatures (near 11 K) are evident in Fig. 1. The peaks shift to lower temperatures as the frequency is decreased, suggesting a thermally activated motion. For dipolar relaxation, the peak occurs when the motion correlation frequency ω_c is 1.6 times the resonance frequency ω.[8,15] In Fig. 4, the resonance frequency $f \equiv \omega/2\pi$ is plotted as a function of the reciprocal temperature of the peak. The three data points are from the peaks at 9 and 380 kHz and at 5 MHz. The straight-line fit indicates that the motion
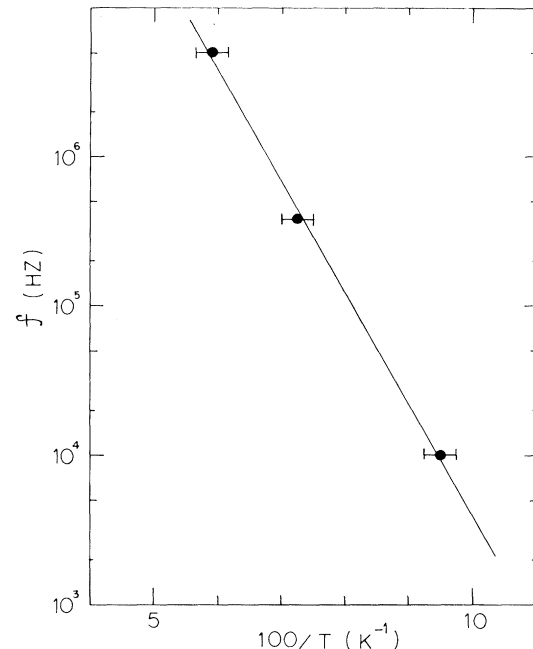

FIG. 4. Relaxation map of the peaks evident in Fig. 1 for T_{1D}^{-1} and for T_1^{-1} at 0.38 and 5.0 MHz. Each point corresponds to the temperature of maximum relaxation rate at one of the three frequencies. The straight line is a fit by $f = f_0 e^{-E/kT}$ with $f_0 = 1 \times 10^{11}$ Hz and $E/k = 172$ K.

is thermally activated, in fact, with an activation energy E/k of 172 K.

The absence of the peaks in the high-frequency data may be due to a well-known prediction of simple relaxation theories: $(T_1^{-1})_{max} \sim \omega^{-1}$.[8,15,19] Indeed, the peak relaxation rates at the three lower frequencies follow this prediction, at least qualitatively. Hence, the peaks at 21.3 and 58.5 MHz may simply be obscured. However, the relaxation peaks at the two highest frequencies are predicted from Fig. 4 to occur in phase II. It may be that the thermally activated motion only occurs in phase III, or only at low temperatures (see below).

What kind of motion would be thermally activated in an incommensurate solid? If the distortion wave were pinned by impurities or defects, thermally activated hopping of the distortion would occur. However, a broad distribution of activation energies would be expected, in disagreement with the relatively sharp relaxation peaks shown in Fig. 1. In Bruce's study[2] of distortion-wave pinning by discrete lattice effects, he predicted a transition from pinned solitons at low temperatures to truly gapless distortion waves at higher temperatures. It is tempting to interpret the thermally activated motion seen in biphenyl as motions in Bruce's intrinsically pinned phase. However, Bruce's pinning is expected to occur in the regime of dilute solitons, while the distortion in biphenyl is approximately sinusoidal (in phase III, only diffraction satellites up to third order could be observed[7]). Nevertheless, the evidence reported here for gapless phasons at high temperatures (20 to 40 K) and for thermally activated motions (hence, pinned distortions) at low temperatures agrees qualitatively with Bruce's prediction.

The thermally activated fit in Fig. 4 may be extrapolated to low temperatures: One finds that $\omega_c \sim 10^{-3}$ s^{-1} at 5 K. Biphenyl is known to remain incommensurate down to 1.6 K,[7] and is rare in not having a known commensurate ground state. Let us suppose that a commensurate phase were thermodynamically stable below 5 K. The correlation time of the thermally activated motion is longer than 10^3 s below 5 K; 10^3 s is the usual time scale of laboratory experiments. Conventional glasses (e.g., window glass) are (metastable) phases in which some important correlation time exceeds laboratory time scales, which produces a frozen-in disorder. Similarly, the incommensurate-commensurate transition below 5 K might be *kinetically inhibited*, which causes biphenyl to exist as an incommensurate *glass* at low temperatures. Of course, the nature of the thermally activated motion and whether it is intimately involved in any transition to a commensurate structure are not known.

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