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Enhancement of (^{14}N) Quadrupolar Relaxation in the One Dimensional Conductor $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\cdot 3.2\text{H}_2\text{O}$ Due to Lattice Fluctuations above the Peierls Transition

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The spin-lattice relaxation T_1 of $^{14}\text{N}(I=1)$ nuclei in a single crystal of the mixed-valency platino-cyanate $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\cdot 3.2\text{H}_2\text{O}$ (KCP) quasi-one dimensional conductor has been measured in the temperature domain from room temperature down to the 3-D Peierls ordering below 120 K. A rapid increase of the quadrupolar relaxation is observed below 220 K which follows the power law $1/T_1 \propto r^{-1/2}$ where $r = (T - T_p)/T_p$. This behaviour is explained in terms of the critical slowing down of lattice fluctuations with a Landau-Ginzburg theory. The square root critical divergence of T_1^{-1} is the signature of the harmonic regime for the order parameter fluctuations. The enhancement of T_1^{-1} and the very wide 3-D critical width can be explained by the strong anisotropy of correlation lengths in this Q-1-D conductor.

§1. Introduction

Spin lattice nuclear relaxation time measurement has proved to be a rewarding experimental technique for the study of precursor regimes developing above the onset of three-dimensional (3D) ordering in quasi-1-D (Q-1-D) conductors.¹⁾

Most of the NMR work has been devoted so far to the experimental investigation of the fluctuation regimes in the organic cation radical salts belonging to the D_2X series.²⁾ This family of 1-D conductors (D=organic cation radical, X=pseudo halogen anion) displays a variety of ground states (Spin-Peierls, Spin Density Wave, Superconductivity) depending on parameters such as chemical species, high pressure or the value of the external magnetic field.¹⁾ However, for these Q-1-D conductors the electron-phonon coupling is rarely the dominant interaction for the establishment of 3-D ordering at low temperature (with the exception of $\text{TMTTF}_2\text{PF}_6$ -like materials) and precursor effects in a Peierls system could not

be studied.

Quite generally, spin-lattice relaxation is due to the exchange of energy between nuclear spins and the energy reservoir (conduction electrons, lattice, etc.). This process is achieved through local random fields seen by nuclei coupled to either magnetic moments or quadrupolar moments. The relaxation rate T_1^{-1} is thus given by:³⁾

$$T_1^{-1} = C^{st} \sum_q \frac{kT}{\omega_n} \chi''(\mathbf{q}, \omega_n), \quad (1)$$

where $\chi''(\mathbf{q}, \omega_n)$ is the imaginary part of the susceptibility related to the random field and ω_n is the nuclear Larmor frequency. For 1-D conductors, excitations contributing most to T_1^{-1} are those accompanied by electron-hole excitations of low energy¹⁾ (i.e. $\mathbf{q}=0$ and $2k_F$ in the \mathbf{q} -summation of eq. (1)). As already discussed in previous studies of 1-D conductors the $2k_F$ component contributes dominantly at low temperature. For organic conductors of the D_2X series the major source of intrinsic spin-lattice relaxation (besides the extrinsic CH_3 -reorientation contribution) comes from the modulation of the hyperfine coupling between itinerant electrons and nuclear spins of the molecules (^1H , ^{77}Se , ^{13}C). T_1^{-1} data have

[†] This article is dedicated to the memory of Gen Soda who started this study while he was staying at Orsay (1974-1976). Gen Soda died in an accident 19 February 1980.

been used to show that the $2k_F$ component of the spin susceptibility of conductors such as $\text{TMTSF}_2\text{PF}_6$ or $\text{TMTSF}_2\text{ClO}_4$ exhibits a power-law temperature divergence which becomes clearly visible below 30 K. The exponent is typical of a 1-D behaviour ($\gamma_{1D} \sim 1$).⁴⁾

The study of the Peierls precursor regime by NMR has not received that much attention. The purpose of the present article is to show how lattice precursor effects can be detected by NMR investigations and how the interpretation fits into the framework of the theory of critical effects at low dimensionality.

The prototype material showing all signs of the Peierls distortion and of a giant Kohn anomaly in the phonon spectrum is the mixed valency platinum complex $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 3.2\text{H}_2\text{O}(\text{KCP})$.⁵⁾ The main feature of KCP is the columnar stacking along the c -axis of square planar $(\text{CN})_4$ ligands comprising each a Pt atom in the center of the square. The distance of 2.88 Å between Pt atoms along the stacking axis is only slightly larger than the Pt-Pt distance in metal (2.77 Å). Consequently, d_z^2 orbitals of Pt atoms overlap strongly along the c -direction and form an energy band. In principle such a band should be filled by two electrons given by each Pt atom. However, it is only 85% filled up to the wave vector $k_F = 0.85c^*$ on account of the presence of bromine atoms giving rise to Br^- ions. Abundant X-ray and neutron scattering experiments have been devoted to the study of this material.⁶⁾ They have shown the onset of a periodic lattice distortion (PLD) below 120 K characterized by a wave vector $(\pi/a, \pi/a, 2k_F)$. Furthermore, X-ray diffuse scattering experiments have revealed the existence at $T = 300$ K of a diffuse streaking perpendicular to the c^* -axis which has been attributed to a 1-D modulation of the underlying lattice.⁷⁾ X-ray are not able to provide informations relative to the dynamics of the modulation. The distance in q -space between diffuse lines and the lines of Bragg spots allows a very precise determination of the Fermi wave vector, leading to $2k_F = 0.3(\pi/c)$ ($c = 2.88$ Å). This value is in agreement with the band filling inferred from chemical considerations and established the proof for the Peierls mechanism in this 1-D conductor. In addition,

intense elastic neutron scattering has been observed at $q = (0, 0, 2k_F)$ even at room temperature.⁶⁾ On cooling down the growth of the elastic intensity at $(\pi/a, \pi/a, 2k_F)$ has indicated the occurrence of transverse coherence. Intensities scattered around $(0, 0, 2k_F)$ and $(\pi/a, \pi/a, 2k_F)$ are about equal at 200 K. Below 200 K the $(\pi/a, \pi/a, 2k_F)$ scattering is dominant but the 1-D $(0, 0, 2k_F)$ scattering which diminishes below 120 K (the 3-D ordering temperature) remains finite. The absence of truly established long range order has been attributed to lattice imperfections. Two origins can be given to the elastic scattering:⁶⁾ a Peierls distortion existing at room temperature or the existence of low frequency critical Peierls fluctuations. The limited resolution of neutron experiments prevented the exact determination of the origin. The study of the quadrupolar relaxation of ^{14}N nuclei belonging to the $(\text{CN})_4$ square planes is "a priori" a good way to check for the latter possibility. No itinerant electron density exists on nitrogen atoms, thus ^{14}N spins ($I = 1$) should relax to the lattice via the modulation by lattice vibrations of the electric field gradients on nitrogen sites. Since $(\text{CN})_4$ ligands are rigidly coupled to Pt of the conducting chains the measurement of ^{14}N spin-lattice relaxation should provide a very direct probe for the existence of critical fluctuations.⁸⁾ The role of Peierls critical fluctuations on the quadrupolar relaxation has already been reported in another Q-1-D conductor,⁹⁾ $\text{Rb}_{0.3}\text{MoO}_3$ showing a Peierls transition at 181 K. However, the situation is slightly more complicated with this conductor as two mechanisms contribute together to the relaxation of ^{87}Rb ($I = 3/2$) spins: the hyperfine and the quadrupolar relaxation.

§2. Experimental Results

The single crystal KCP sample was oriented with the c -axis parallel to the external magnetic field. Temperature between 300 and 120 K were achieved using a dry N_2 -gas flow system. The ^{14}N NMR signal was obtained by a conventional spin echo technique using an analog box-car integrator. The spectrometer was tuned at a frequency of 9.9 MHz and the center of the resonance occurred at 36.2 kOe.

The observed NMR corresponds to the high field quadrupolar satellite of the $^{14}\text{N}(I=1)$ doublet. Given the orientation of the static magnetic field and the cylindrical symmetry of electric field gradients, q , the shift of the line leads to $(e^2qQ/h)=1650$ kHz. The temperature independent inhomogeneous broadening ($\Delta H=300$ Oe) of the line can be understood in terms of the static disorder introduced by Br^- ions and frozen H_2O molecules.¹⁰ Spin-lattice relaxation was obtained by a $\pi/2$ comb- τ - $(\pi/2)$, π pulse sequence varying the delay τ . The data for the half recovery rate T_0^{-1} instead of T_1^{-1} are displayed in Fig. 1. The minimum occurring around 220 K indicates a change of regime for the nuclear quadrupole relaxation. At high temperature the relaxation rate is increasing with temperature. This temperature dependence is expected for quadrupolar relaxations induced by a spin-phonon coupling. Since this temperature domain is higher than the Debye temperature of KCP the second order Raman process leading to $T_1^{-1} \propto T^2$ should dominate.³ The data on Fig. 1 are obviously not accurate enough to ex-

tract a well characterized T -dependence between 220 and 280 K. However, they are in qualitative agreement with the existence of the Raman process. Below 220 K the T_1^{-1} temperature dependence cannot be explained by spin-phonon coupling in regular solids. The divergence observed when approaching the Peierls transition must be ascribed to a critical slowing down of the lattice fluctuations.⁸⁾

§3. Discussion

In the following we will be mainly concerned with the origin of the strong enhancement of T_1^{-1} that emerges below 200 K. The log-log plot of the T_1^{-1} data versus $T-T_c$ in figure 1 clearly supports a power law behaviour of the form $T_1^{-1} \propto ((T-T_c)/T_c)^{-\nu}$. The best fit of the data gives $\nu=1/2 \pm .05$ with $T_c \approx 117$ K. It is well established from several experiments that the temperature of the Peierls "ordering" in KCP occurs around $T_p \approx 110$ -120 K, showing the possible relevance of the 3D "ordering" on the enhancement of T_1^{-1} . In fact, such a critical profile for the quadrupolar relaxation is reminiscent of what is commonly observed near incommensurate structural phase transitions,^{8,11)} like the one taking place in the ferroelectric crystal Rb_2ZnCl_4 for example.¹¹⁾ The exponent $\nu=1/2$ is mean field like and is well known to result from strongly damped 3D harmonic fluctuations which affect the relaxation via the so-called direct process. One must note however that the critical width associated with this type of enhancement namely, $\Delta_H = ((T_H - T_c)/T_c)$ is usually of the order of 10^{-2} or so in these compounds.¹¹⁾ This is clearly much smaller than the one observed here for KCP. Indeed, from the figure 1 $T_H \approx 200$ K (i.e. $\Delta_H \sim 1$). It is well known that strong spatial anisotropies in the correlation lengths can significantly increase the observable width of critical fluctuations around T_c .^{12,13)} This is especially relevant here since the Peierls transition in KCP is known to be a classical example of a system of weakly coupled incommensurate charge density wave chains.⁶⁾ Indeed, the $1\text{D}-2k_F$ phonon coupling to the $2k_F$ charge density wave instability of the 1D electron gas already dominates above room temperature with very weak transverse correlations that level off at T_p .⁶⁾ In

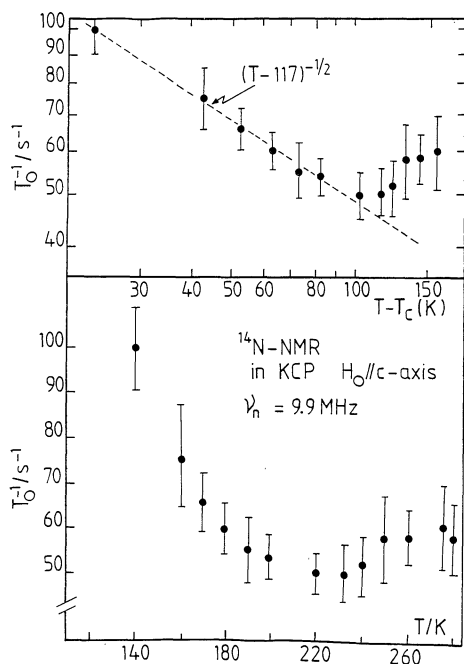


Fig. 1. Temperature dependence of the ^{14}N magnetization half recovery rate (bottom). Log-log plot of the half recovery rate versus $T-T_c$ with the value of $T_c=117$ K (top).

addition, from neutron scattering experiments,⁶⁾ the correlation lengths associated to the superstructure wave vector $(\pi/a, \pi/a, 2k_F)$ at T_{fl} are highly anisotropic namely, $(\xi_x^0, \xi_y^0, \xi_z^0) \approx (3 \text{ \AA}, 3 \text{ \AA}, > 300 \text{ \AA})$. From resolution limitations, only a lower bound of ξ_z^0 can be given. The small ratio $\xi_{x,y}^0/\xi_z^0 \ll 1$ is consistent with a large temperature domain where $1D-2k_F$ lattice precursors along the z direction should dominate. Actually, NMR Knight shift measurements on ¹⁹⁵Pt have shown the existence of a 1D pseudo-gap in the density of states at the Fermi level.¹⁴⁾ This had led to infer that the characteristic or the mean field temperature T_p^0 for the apparition of 1D fluctuations should be around 600 K or so!. As the non singular unrenormalized $2k_F$ phonon frequency $\omega_{2k_F} \sim 80 \text{ K}^{(6)}$ we have $2\pi T_p^0 \gg \omega_{2k_F}$ which means that a strong adiabaticity prevails between the lattice and the electron gas system. It follows that a classical fluctuating Peierls order parameter is a well defined quantity below T_p^0 .

The Peierls instability is incommensurate in KCP and the order parameter has two components thereby allowing amplitude and phase fluctuations. In the purely 1D regime, the amplitude fluctuations are strongly anharmonic. The repulsive potential (Coulombic) interchain coupling, though weak, in amplitude will favor an antiphase ordering of the order parameter in the transverse direction. The

growth of the correlation length $\xi_{x,y}$ will mark the onset of a dimensionality crossover for fluctuations which in turn restores the harmonicity of the order parameter fluctuations. The harmonicity persists as long as ξ_x or ξ_y are not too large otherwise non-mean field like critical effects take place within the so-called Ginzburg critical width Δ_G .¹⁵⁾

The latter will always satisfy the inequality $\Delta_G < \Delta_H$.

Given the strong adiabaticity of the electron-phonon system precursor to the transition, the lattice fluctuations can be considered classically and an important contribution to the NQR relaxation will come from the direct process. According to Zummer and Blinc¹⁾ for example, the contribution to T_1^{-1} becomes in this case:

$$T_1^{-1} = \text{cst} |T'(l)|^2 2T \int d_q^d \frac{\chi''(\mathbf{q}, \omega)}{\omega}. \quad (2)$$

$T'(l)$ is the first derivative of the electric field gradient tensor at the site l . $\chi''(\mathbf{q}, \omega)$ is the imaginary part of the retarded correlation function for the classical lattice displacement at wave vector \mathbf{q} and frequency ω . Applying the dynamic scaling hypothesis^{2,8,16)} to the three quantities $\{d_q^d, \chi''(\mathbf{q}, \omega)$ and ω , the latter will scale with the coherence length ξ to some characteristic power (exponent). We will get for $\mathbf{q} \approx \mathbf{q}_0 = (\pi/a, \pi/a, 2k_F)$ and $d=3$ dimensions:

$$T_{1cr}^{-1} = 2Cst |T'(l)|^2 T_p \Gamma \frac{r^{3v-\gamma-Zv} \int_0^{c_i} d(\xi_x q_x) d(\xi_y q_y) d(\xi_z q_z) \chi''(\mathbf{q} \cdot \xi, \Gamma r^{-Zv} \omega)}{(\Gamma r^{-Zv} \omega)},$$

$$T_{1cr}^{-1} \propto \frac{r^{3v-\gamma-Zv}}{(\xi_x^0 \xi_y^0 \xi_z^0)} \quad (r < 1), \quad (3)$$

where $r = (T - T_p)/T_p$, Γ is the order parameter damping constant and $c_i > 1$ ($i=x, y, z$) for $r < 1$. A Peierls order parameter is a non-conserved quantity and therefore Γ will be q independent. ν , γ and Z are respectively the critical exponents of the correlation length ($\xi_i = \xi_i^0 r^{-\nu}$) susceptibility ($\chi'' \propto r^{-\gamma}$) and fluctuation relaxation rate ($\omega \propto r^{Zv}$). Given the observed anisotropies for the ξ_i^0 , ($\xi_i = \xi_i^0$ at $T \approx T_{fl}$), an harmonic time-dependent Landau-Ginzburg approach is justified below T_{fl} . This

leads to exponents¹⁶⁾ $\nu=1/2$, $\gamma=1$, $Z=2$ ($\Gamma = cst$) and to the classical profile

$$T_1^{-1} \propto \frac{r^{-1/2}}{(\xi_x^0 \xi_y^0 \xi_z^0)}, \quad (r < 1) \quad (4)$$

for $r < 1$. Owing to the strong anisotropies of ξ_i^0 in KCP, the amplitude of T_1^{-1} will be enhanced compared to the isotropic case by the factor $(\xi_z^0)^2 / (\xi_y^0 \xi_x^0) \sim 10^4$. Such a value can explain why Δ_H is much larger than the harmonic width found in more isotropic sys-

tems such as the ferroelectric compound Rb_2ZnCl_4 ¹¹⁾ and other similar systems.^{8,15,17)} Roughly speaking, if we assume that the differences between Δ_H come essentially from the ξ_i^0 's, then this implies the value $\xi_{x,y,z}^0 \approx 30 \text{ \AA}$ or so for a 3D system like Rb_2ZnCl_4 . This characteristic length is consistent with the typical Ginzburg critical width $\Delta_G \sim 10^{-4}$ found in ferroelectric systems (see ref. 15).

The anisotropy in the ξ_i^0 's does not only affect the direct process-type of quadrupolar relaxation but also the relaxation contribution coming from the second order Raman process.⁸⁾ According to refs. 8 and 11, the Raman contribution is non-singular as we approach the transition namely, $T_1^{-1} \propto (\xi^0)^{-5} T^2$. However, for an anisotropic system like KCP, this contribution is enhanced by a factor $[\xi_0^0 \xi_x^0 / \xi_z^0]^2 \approx 10^7$ at T_f . Such a huge factor may be responsible for the increase of T_1^{-1} at $T > T_f \sim 200 \text{ K}$ (see Fig. 1). This will mask the 1D fluctuation effects on the quadrupolar relaxation that should take place above T_f . Actually, 1D amplitude and phase Peierls fluctuations would give, via direct processes, contributions of the form $T_1^{-1} \sim |(T - T_0) / T_0|^{-3/2}$ ($T > T_0$) and $T_1^{-1} \sim (T / T_0)^{-1}$ ($T < T_0$). Here, $T_0 \sim T_p^0 / 3$ is a characteristic temperature for the apparition of phasons.¹⁾ None of these profiles seem to be relevant to the observation. One must note however, that in KCP, $T_0 \approx 200 \text{ K} \approx T_f$, which means that only 1D amplitude fluctuations are relevant for $T_f < T < T_p^0$.

The existence of precursor effects above the Peierls transition is also suggested by the early measurements of ^{195}Pt ($I=1/2$) spin-lattice relaxation rates.¹⁴⁾ The ^{195}Pt relaxation rate is anomalously large and the enhancement relative to a Korringa mechanism derived from Knight shift data increases when T decreases. Therefore, the divergence of the Korringa enhancement factor $(1/T_1)_{\text{Pt}}^{\text{exp}} / (1/T_1)_{\text{Pt}}^{\text{Korringa}}$ observed at low temperature¹⁴⁾ looks quite similar to the divergence of the quadrupolar relaxation rate presented in the present study. ^{195}Pt and ^{14}N resonances probe respectively the

electronic and lattice effects of the precursor fluctuations.

In conclusion, the study of the quadrupolar relaxation of ^{14}N nuclei in the 1-D conductor KCP has demonstrated that Peierls lattice fluctuations strongly contribute to the spin-lattice relaxation in the temperature domain above the Peierls transition. The square root divergence which is revealed below 220 K is fairly well understood in terms of the effect of the critical slowing down of the fluctuations on the spin-phonon direct process.

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