Interplay between phase defects and spin polarization in the specific heat of the spin density wave compound (TMTTF)$_2$Br in a magnetic field

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Equilibrium heat relaxation experiments provide evidence that the ground state of the commensurate spin density wave (SDW) compound (TMTTF)$_2$Br after the application of a sufficient magnetic field is different from the conventional ground state. The experiments are interpreted on the basis of the local model of strong pinning as the deconfinement of soliton-antisoliton pairs triggered by the Zeeman coupling to spin degrees of freedom, resulting in a magnetic field induced density wave glass for the spin carrying phase configuration.

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Metastability results from energy minima in a system phase space, separated from each other by energy barriers. In some complex systems such as spin glasses, the number of metastable states and the scaling of the energy barriers with the system size are such that ergodicity is broken, meaning that time averaging is not equivalent to ensemble averaging because the system is “trapped” in a valley of the energy landscape. Metastability is also found in model systems such as molecular magnets or Josephson junctions, described by an energy potential $V(\phi)$ as a function of a single degree of freedom $\phi$. We investigate below experimentally and theoretically the residual degrees of freedom of a spin density wave (SDW) at very low temperature in a magnetic field, interpreted as the properties of a classical potential $V(\phi(y))$ for the SDW phase $\phi(y)$ at the coordinate $y$, along the chain of a strong pinning impurity.

Below the Peierls transition temperature, charge density waves (CDWs) and SDWs in quasi-one-dimensional (quasi-1D) compounds are characterized by a spatial modulation of the electronic density (or spin) along the chains. The phase profile is the result of a compromise between the elastic energy that penalizes large phase gradients, and the pinning energy that tends to fix the phase at the strong pinning centers. These two ingredients of the Fukuyama-Lee-Rice model 1 lead to metastability as the result of collective pinning. Collective pinning is however frozen below a glass transition of order $\sim 50$ K, as shown by dielectric susceptibility experiments 2. At very low temperature, the residual degrees of freedom in a zero magnetic field correspond to the local defects of the local model of strong pinning 3,4,5. Larkin 4 and Ovchinnikov 5 have shown that a single strong pinning impurity leads to a bound state of an electron-like soliton and a hole-like antisoliton. This results in a potential $V(\phi(y))$ with multiple minima 6, leading to slow relaxation in agreement with the very low temperature heat relaxation experiments 6.

In order to explore the role of a magnetic field, we choose the compound (TMTTF)$_2$Br with a sufficiently narrow spectrum of relaxation times because of its commensurate (antiferromagnetic) ground state 7,10. This allows a systematic study of the equilibrium energy relaxation over almost one decade in temperature and a direct comparison to the local model of strong pinning without introducing an additional time scale related to ageing 7,11.

The specific heat of about 60 mg of a (TMTTF)$_2$Br salt was measured at CRTBT-Grenoble in a dilution cryostat set-up under magnetic field up to 7 T. This compound was previously investigated in zero field in a similar temperature range 8. We use a standard relaxation method 8,10, but in contrast to previous experiments, the specific heat is determined at equilibrium, once the heat relaxation regime $\Delta T(t)$ as a function of time $t$, obtained after a long heat input, becomes exponential. This internal relaxation time $t_{in}$ reaches up to more than $10^4$ s at the temperature $T = 60$ mK and at high field. This technique requires probing times of about $3 \div 4 t_{in}$ for the determination of the time constant $\tau_{eq}$ of the exponential relaxation for $t > t_{in}$, and hence extremely stable field supply and temperature regulation. The equilibrium specific heat $C_{eq}$ reported on Figs. 1 and 2 is obtained from the relation $C_{eq} = \tau_{eq}/R_{hl}$, where $R_{hl}$ is the heat link resistance between the sample and the regulated cold sink, measured at equilibrium under permanent power supply (more details will be published separately).

The temperature dependence of the specific heat $C_p(T)$ is shown on Fig. 1 for different values of the magnetic field. We find experimentally a specific heat proportional to $1/T^2$, with a prefactor varying by almost two orders of magnitude when the magnetic field increases from $h = 0$ T to $h = 7$ T. This temperature variation is interpreted 7,11 as the high temperature tail of a Schottky due to two level-like systems. The specific heat of a concentration $A$ of two-level systems with an energy splitting...
Specific heat follows $C_p^{(2)}(h)$ upon decreasing the magnetic field below $h_c$, and remains on branch 2 if the magnetic field is further cycled above $h_c$. This signals that a magnetic field $h > h_c$ induces a new ground state that we identify below as a density wave glass. Branch 1 is recovered with the following history: i) the sample is reheated in zero field from 90 mK up to about 20 K ii) once the sample is cooled down, the magnetic field is increased up to 1.5 T and decreased again to 0.2 T. The raw experimental data are well fitted by $C_p^{(1,2)}(h,T) = \left[C_0^{(1,2)} + C_p^{(0)}(\mu h/k_BT)\right] \text{mJ/mol K}$ for branches 1 and 2, where $h$ is in Tesla and $T$ in Kelvin, and with $C_0^{(1)} = 120 \text{ mJ/mol K}$, and $C_0^{(2)} = 404 \text{ mJ/mol K}$. We find $C_p^{(0)}(\mu h/k_BT) \simeq 190(h/T)^2 \text{ mJ/mol K}$ for $k_BT$ much larger than $\mu h$.

The internal equilibrium time $t_{\text{eq}}$ follows an activated regime $t_{\text{eq}} = \tau_0 \exp(E_A/T)$ with an activation energy $E_A \simeq 0.50 \text{ K}$ and a magnetic field-dependent attempt time $\tau_0$ of the order of a few seconds (see Fig. 3). In zero field, we find an excellent agreement with a previous determination of the activation energy, obtained from the spectrum of relaxation times. The activated behavior is in agreement with the local model of strong pinning that we consider now.

The effective 1D Hamiltonian for the phase $\varphi(y)$ of the

$\Delta$ is $C_p^{(0)}(\Delta/k_BT) = A(\Delta/k_BT)^2/[2 \cosh(\Delta/2k_BT)]^2$, that behaves like $C_p^{(0)}(\Delta/k_BT) \simeq A(\Delta/2k_BT)^2$ for $k_BT$ large compared to $\Delta$. The temperature dependence of the specific heat is well described by $C_p^{(0)}(\mu h/k_BT)$, with a splitting $\Delta = \mu h$. The value of $\mu \simeq 0.011\mu_B$ (with $\mu_B$ is the Bohr magneton of an electron) deduced from the fit on Fig. 1 is approximately one order of magnitude smaller than the SDW amplitude measured by NMR. This is because solitonic excitations involve a distribution of spins with a staggered orientation, with a net magnetic moment smaller than the moment of an individual spin (see Fig. 5). We have chosen the fit leading to the smallest value of $A \approx 60 \text{ J/mol K}$ compatible with experiments. This results in a huge number of defects induced by the magnetic field (approximately 8 defects per unit cell) that cannot be explained by impurities. Here we relate the magnetic field specific heat to spin degrees of freedom in a density wave (DW) glass, not to the phase excitations of bisolitons in the local model of strong pinning where the number of phase defect would be equal to the number of pinning centers. The fit of the temperature dependence of the specific heat in zero field leads to a concentration of defects of approximately 20%. This concentration is consistent with the Ovchinnikov estimate in (TMTSF)$_2$PF$_6$, but is however too large to be ascribed to extrinsic impurities.

We report for the first time metastability induced by the magnetic field at a fixed temperature $T = 92 \text{ mK}$ (see Fig. 2). The sample that has not “seen” the magnetic field follows the branch $C_p^{(1)}(h)$ and remains on branch 1 if the applied magnetic field does not exceed $h_c \sim 5.5 \text{ T}$. If the magnetic field increases above $h_c$, the
SDW takes the form\textsuperscript{14,15,16,17}:
\[
\mathcal{H} = \frac{v_F}{4\pi} \int dy \left( \frac{\partial \varphi(y)}{\partial y} \right)^2 + w \int dy \left[ 1 - \cos \varphi(y) \right],
\]
where \(y\) is the coordinate along the chain, \(v_F\) the Fermi velocity, \(w\) the commensuration potential. The excitations in the absence of impurities are pairs of \(\pm 2\pi\) solitons and antisolitons, the phase of which winds by \(\pm 2\pi\) within a correlation length \(\xi = \sqrt{\hbar v_F/2\pi w}\). A SDW is viewed as the superposition of two out-of-phase CDWs for spin-up and spin-down electrons, and the SDW pinning energy is obtained to second order as\textsuperscript{14,15,16,17}:
\[
\mathcal{H}_{\text{imp}} = \sum_i v_i \cos \left[ 2 \left( Qy_i + \varphi_i \right) \right],
\]
where the sum runs over all strong pinning impurities at position \(y_i\) along the chain. The phase field is \(\varphi(y) = \varphi_\uparrow(y) - \varphi_\downarrow(y) + \pi\), where \(\varphi_\uparrow(y)\) and \(\varphi_\downarrow(y)\) are the spin-up and spin-down phase fields. The residual specific heat at low field of 120 mJ/mol K in \(C_p^{(1)}(h, T)\) is related to metastability due to spinless bisolitons (bound state of a soliton and an antisoliton)\textsuperscript{14,15,16,17}. The phase profile \(\varphi_0(y)\) of a bisoliton is\textsuperscript{14,15,16,17}:
\[
\tan \left( \frac{\varphi_0(y)}{4} \right) = \tan \left( \frac{\psi}{4} \right) \exp \left( -\frac{|y-y_i|}{\xi} \right).
\]
The ground state of a bisoliton in the absence of a magnetic field is at energy \(E_0\), separated by a barrier from a metastable state at energy \(E_0 + \Delta E\), with \(\Delta E = 4E_S = 16\sigma\xi\), where \(E_S\) is the energy of a \(\pm 2\pi\) soliton in the pure system. This defines an effective two-level system\textsuperscript{14,15,16,17}.

A Zeeman coupling to the magnetic field is included now through \(\mathcal{H}_h = -\mu_h \int dy [\rho_\uparrow(y) - \rho_\downarrow(y)]\), where the electronic density \(\rho_\sigma(y)\), with \(\sigma = \uparrow, \downarrow\), is defined by\textsuperscript{14,15,16,17}:
\[
\rho_\sigma(y) = \rho_0 \left[ 1 + Q^{-1} \frac{\partial \varphi_\sigma(y)}{\partial y} \right] + \rho_1 \cos (Qy + \varphi_\sigma(y)),
\]
where \(Q\) is the SDW wave-vector, \(\rho_0\) is the electronic charge per unit length in the absence of deformation. The term containing \(\rho_1\) is relevant to local pinning, but averages to zero in the Zeeman energy integrated over \(y\) because of the short scale oscillations at the Fermi wave-length.

A \(2\pi\) soliton in the spin-up field \(\varphi_\uparrow(y)\) and a \(-2\pi\) soliton in the spin-down field \(\varphi_\downarrow(y)\) both carry a net spin-up because their energy decreases by \(2\pi\mu_h\rho_0Q^{-1}\) in a magnetic field \(h\). In the absence of impurities, the SDW ground state is unstable against the nucleation of pairs of solitons and antisolitons carrying a net spin-up if the gain in the Zeeman energy exceeds the soliton energy \(E_S\), a condition equivalent to \(h > h_c\), with \(h_c = 2Qh_S/\pi\mu_0\). An upper bound to the temperature of the maximum of the Schottky anomaly in a zero field is \(T_{\text{max}} \simeq 10 \div 20\) mK, leading to \(4E_S \simeq 2.4T_{\text{max}}\), so that \(h_c = 4E_S/\mu\) is lower than \(\sim 2.2\div 4.3\) T is compatible with the cross-over magnetic field obtained experimentally.

Now, we show how deconfined pairs of solitons and antisolitons are nucleated from the strong pinning impurities. A spinless bisoliton corresponds to \(\varphi_\uparrow(y) = \varphi_\downarrow(y)\) and \(\pi - \varphi_\downarrow(y) = 0\) for all values of \(y\) (see Eq.\textsuperscript{14,15,16,17} for \(\varphi_0(y)\)). Alternatively, the field \(\varphi_\downarrow(y)\) can be excited: \(\varphi_\uparrow(y) = 0\) and \(\pi - \varphi_\downarrow(y) = \varphi_0(y)\) for all values of \(y\). On the other hand, a maximally spin polarized bisoliton is obtained
The spinless bisolitons restore a finite specific heat. In a degenerate two-level system with a vanishingly small magnetic field, the magnetic energy is opposite to the spin degrees of freedom on the solitons and antisolitons. The pinning energy is such as to reproduce the experimental activation energy $E_A \simeq 0.5$ K (see Fig. 3). The figures show the potential energies of a bisoliton with no additional soliton-antisolon pair (solid line, red), with a soliton for $y < y_i$, and an antisoliton for $y > y_i$ (short dashed, blue), and with an antisoliton for $y < y_i$ and a soliton for $y > y_i$ (long dashed, green).

by reversing the spin in the part of the soliton corresponding to $y > y_i$, in such a way that $\varphi_1(y) = \varphi_0(y)$ and $\pi - \varphi_1(y) = 0$ for $y < y_i$, and $\varphi_1(y) = 0$ and $\pi - \varphi_1(y) = \varphi_0(y)$ for $y > y_i$. A sequence generating a deconfined soliton-antisolon pair starts from the minimum (1) with a small value of $\psi_i/2\pi$ (see Fig. 3). The phase $\psi_i$ at the position of the impurity crossed over to the other minimum (2) with $\psi_i/2\pi \simeq 1$, and the soliton-antisolon pair deconfines by relaxing to the minimum (3). The process can then be iterated, inducing the same random configuration of the SDW phase as in a DW glass [2].

The bisoliton contribution in low field (see Fig. 3) is obtained by assuming a population of spinless and spin polarized bisolitons in thermal equilibrium. The specific heat of the spin-up bisolitons with a magnetic moment parallel to the applied magnetic field vanishes at the magnetic field $h_c$ (see Fig. 3). For this value of the magnetic field, the magnetic energy is opposite to the Larkin-Ovchinnikov level splitting in zero field, resulting in a degenerate two-level system with a vanishingly small specific heat. The spinless bisolitons restore a finite specific heat (see the total contribution of the bisolitons on Fig. 3). If the field is reduced from a large value, the pairs of solitons and antisolitons annihilate reversibly for $h > h_c$, and the phase is trapped at $h = h_c$. The random phase pattern induced by the magnetic field persists if the field decreases back to zero. The spin degrees of freedom on the residual phase defects explain the specific heat of branch 2, larger than the specific heat of branch 1.

To conclude, we have found experimentally a very persistent metastable branch in the magnetic field dependence of the specific heat with a larger specific heat than in the zero field case. We interpreted this observation in terms of the local model of strong pinning coupled to a Zeeman field, in which we find an instability of the SDW ground state with a flat phase towards a DW glass with a random phase configuration. The additional contribution to the specific heat when coming back to zero field is explained by the spin entropy due to the magnetic moments on the phase defects of the DW glass. Interestingly, a moderate pressure induces a transition to an incommensurate phase in the same compound [18], which was explained by the formation of discommensurations.

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[1] H. Fukuyama and P. A. Lee, Phys. Rev. B 17, 535 (1977); H. Fukuyama, J. Phys. Soc. Jpn. 45, 1474 (1978); P. A. Lee and T. M. Rice, Phys. Rev. B 19, 3970 (1979).
[2] D. Starešinić et al., Phys. Rev. B 65, 165109 (2002).
[3] H. Fukuyama, J. Phys. Soc. Jpn. 41, 513 (1976).
[4] A.I. Larkin, Zh. Eksp. Teor. Fiz. 105, 1793 (1994) [Sov. Phys. JETP 78, 971 (1994)].
[5] Yu. N. Ovchinnikov et al., Europhys. Lett. 34, 645 (1996).
[6] R. Mélin et al., Eur. Phys. J. B 26, 417 (2002); R. Mélin, K. Biljaković and J.C. Lasjaunias, Eur. Phys. J. B 43, 489 (2005).
[7] S. Brazovskii and T. Nattermann, Adv. in Physics 53, 177 (2004).
[8] S. Abe, Physica 143 B, 85 (1986).
[9] J.C. Lasjaunias et al., J. Phys. IV France 12 (2002) Pr 9-23; J.C. Lasjaunias et al., J. Phys. Condens Matter 14, 8583 (2002).
[10] J.C. Lasjaunias, R. Mélin, D. Starešinić, K. Biljaković, and J. Souletie, Phys. Rev. Lett. 94, 245701 (2005).
[11] K. Biljaković, J.C. Lasjaunias, P. Monceau, and F. Levy, Phys. Rev. Lett. 67, 1902 (1991).
[12] E. Barthel et al., Europhys. Lett. 21, 87 (1993).
[13] S. Sahling, J.C. Lasjaunias, K. Biljaković and P. Monceau, J. Low Temp. Phys. 133, 273 (2003).
[14] P.F. Tua and J. Ruvalds, Phys. Rev. B 32, 4660 (1985).
[15] Y. Suzumura, T. Saso and H. Fukuyama, Jpn. J. App. Phys. 26, 589 (1987) Supplement 26-3.
[16] I. Tüttö and A. Zawadowski, Phys. Rev. Lett. 60, 1442 (1988).
[17] K. Maki and A. Virozdbek, Phys. Rev. B 39, 9640 (1989).
[18] B.J. Klemme et al., Phys. Rev. Lett. 75, 2408 (1995).