Commensurate and Incommensurate Spin-Density Waves and a Modified Phase Diagram of the Bechgaard Salts

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We have performed transport and ^{13}C NMR measurements on the sulfur-based Bechgaard salt, $(TMTTF)_2Br$, at different pressures. At low pressures the ground state antiferromagnetism is commensurate with the lattice, while at high pressures many signatures of incommensurate density waves are found. Evidence that the transition, or crossover, between the two regimes is coincident with the suppression of a charge gap induced by coupling of the electronic states to the anion potential is presented.

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The Bechgaard salts are a series of compounds with the empirical formula $(TMTCF)_2X$ (C = Se, S, X = ReO_4, PF_6, FSO_3, etc.) in which an extraordinarily wide variety of cooperative phenomena are manifested, including superconductivity, spin-density waves, order-disorder transitions, magnetic-field-induced transitions, and charge localization [1–3]. Without exception, the ground state of the electronic degrees of freedom in zero magnetic field are either spin Peierls, antiferromagnetic, or superconducting. Which ground state is formed depends on the quantitative details of some microscopic parameters. Thus exchanging selenium for sulfur or using a different anion can be regarded as a means of "tuning" the low-temperature properties [4,5]. The selenium-based salts have a much higher conductivity and tend to form incommensurate spin-density wave (ISDW) ground states at ambient pressure [6]. With 5–10 kbar of pressure, the ISDW transition is suppressed. Leaving the material superconducting [7]. The sulfur-based salts, on the other hand, tend to have much smaller conductivity at room temperature, and enter a charge-localization regime when the sample is cooled below 100–200 K [8,9]. For many cases, a spin gap develops at still lower temperatures [10]. It is identified as a spin Peierls phase, because there is an associated lattice distortion [11].

The charge localization of the sulfur-based salts has been attributed to a significantly stronger coupling to the anionic potential via umklapp scattering [12–14]. The effect is to induce a small dimerization of the molecules along the stacks. A correlation between the size of dimerization and resistivity is well established [8,9], and a common feature is the appearance of a minimum resistivity at $T_\rho \sim 200$ K. Generally, this temperature is considered to give the scale of the dimerization charge gap; below it, only the spin degrees of freedom are relevant. Three-dimensional order in the form of a spin Peierls or antiferromagnetic ground state follows if the transverse coupling is not zero.

Distinctly different physics dominates for the delocalized salts. Here, the umklapp scattering is irrelevant, and the spin-density wave state emerges from a nested Fermi surface. While there are no neutron-scattering measurements of the magnetic order, NMR line-shape analyses indicate that the wave vector is incommensurate with the lattice [15–17]. Observation of nonlinear conductance above a threshold electric field, coincident with motional narrowing of the line shape, is consistent with charge transport via a sliding, incommensurate SDW, with the incommensurability arising from imperfect nesting rather than because of an irrational band-filling factor.

In addition to an exchange of ions or anions, high pressure has also been used to tune the physical properties. Consider, for instance, $(TMTTF)_2Br$, which exhibits a moderate degree of charge localization ($T_\rho \sim 130$ K). Yet, the ground state is antiferromagnetic but commensurate with the lattice [17,18]. With the application of ~25 kbar, the antiferromagnetism is completely suppressed, and the ground state is superconducting [19,20]. Thus pressure is a continuously variable experimental parameter which can be exploited to completely alter the low-temperature properties by varying the importance of imperfect nesting [20,21]. Here, we report on measurements of the transport and ^{13}C NMR line shape for $(TMTTF)_2Br$ (S-Br). As stated above, the material has been previously identified with a commensurate SDW (CSDW) at low temperatures. This is a potentially very interesting system, because the Bechgaard salts, such as $(TMTSF)_2PF_6$ (Se-PF_6), exhibit very striking transport effects as a result of ISDW formation. Thus, S-Br could provide an opportunity for fine-tuning the amount of imperfect nesting from a state where it is unimportant (e.g., at $P = 1$ bar using pressure on the same sample. We show that by application of pressure the effect of the anion potential rapidly diminishes, leading to an associated increase in the ordering temperature T_N. The maximum in T_N [$T_N^{\max} = T_N(P_M)$] appears to be connected closely

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with the pressure at which $T_\rho \rightarrow 0$. The implication is that the coupling of the electrons to the anionic potential lead drives the system commensurate, away from the optimal nesting vector for SDW formation. At pressures $P > P_M$, a nesting model seems to be appropriate, and this manifests itself in the observation of nonlinear conductivity above a threshold electric field, as well as spin-lattice relaxation and line shape more reminiscent of incommensurate SDW's. Based on our observations, we propose a modification of the phase diagram for the broken-symmetry states of the Bechgaard salts.

Although the sulfur-based salts seem to be much more difficult to synthesize than the selenium counterparts, these samples had well-defined faces and, in those used in the magnetic resonance experiments, the angular dependence of the ^{13}C line shape was consistent with single crystals. The transport measurements were carried out using a standard clamp cell arrangement to 14 kbar, and the NMR measurements were conducted in a similar cell, but configured for handling frequencies to 100 MHz.

Resistivity at two different pressures, ~3 and 12 kbar, is shown in Fig. 1. The low-pressure curve exhibits a minimum of the resistivity at $T_\rho \sim 90$ K, and the change in resistivity from 300 K to T_ρ is only about a factor of 2. The onset of the antiferromagnetic ground state is near 20 K and leads to a weak maximum in the derivative of the resistivity with temperature. The contrast with higher pressures, as is well known [19,20], is dramatic. First of all, the conductivity at 300 K increases by more than a factor of 5 on changing the pressure from 1 bar to 10–15 kbar. Also, from 300 K to low temperatures, the data at 12 kbar show that the overall conductivity increase is about two orders of magnitude. This is similar to changes observed in poorer-quality $(TMTSF)_2PF_6$ samples at ambient pressure.

Our phase diagram is summarized in Fig. 2. T_ρ is marked as well as the antiferromagnetic ordering temperature, T_N. Sample cracking problems at ambient pressure often prevent the collection of reliable transport data at 1 bar, so $T_N(P = 1 \text{ bar})$ is established by the onset of the ^{13}C NMR line broadening measured at 75 MHz. The other phase transition temperatures were obtained by the maximum in the derivative of $d(\ln\rho)/d(1/T)$. No evidence for sample cracking was observed at any of the measured pressures. Two regimes, apparently quite distinct, are recognizable. At the low-pressure side ($P < P_M = 5$ kbar), $d(T_N)/dP \sim +1.5$ K/kbar. For $P > P_M$, $dT_N/dP \sim -1$ K/kbar. The maximum ordering temperature of ~22 K is significantly higher than for systems such as $(TMTSF)_2PF_6$, where $T_N = 12$ K. It is not yet clear if T_N is singular at P_M. The possibility that it could be comes from the observation that T_ρ is decreasing extremely rapidly toward 0 K at a pressure extraordinarily close to P_M. To our knowledge, this is the only existing data confirming there is a P_M for the S-Br salt, and that T_ρ vanishes so close to P_M.

The origin of the differences between the two pressure regimes starts to become apparent when field-dependent transport is explored. In Fig. 3, we show a trace of dV/dI vs I for one of the three samples we investigated in the high-pressure regime. What is remarkable is that there is a distinct threshold field [22]; at low pressures only extremely weak non-Ohmicity, indistinguishable from trivial sample heating, was observed. Overall, the nonlinearities we observed appear very similar to those observed for the thoroughly studied $(TMTSF)_2PF_6$. As for Se-PF_6, E_T was found to be independent of temperature for $T \ll T_N$ (the nonlinearities were not investigated above ~7 K because of sample heating problems). The differential conductance increases by a factor of 2 at biases several times threshold, but the threshold field is of order 20–100 times larger in the S-Br sample than in high-quality Se-PF_6 samples. If we attribute the nonlinear conductance to

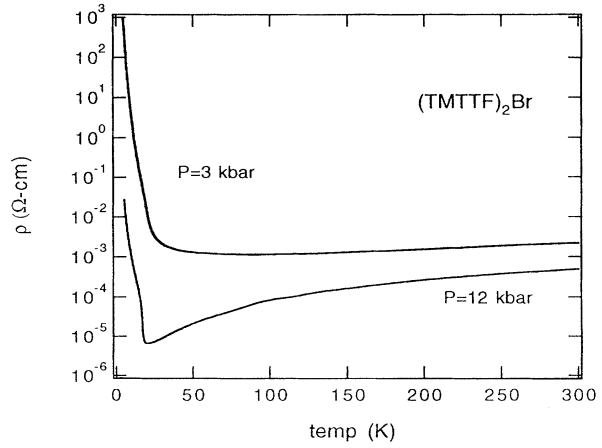

FIG. 1. Resistivity along the highest conductivity direction vs temperature at $P \sim 3$ and 12 kbar for $(TMTTF)_2Br$.

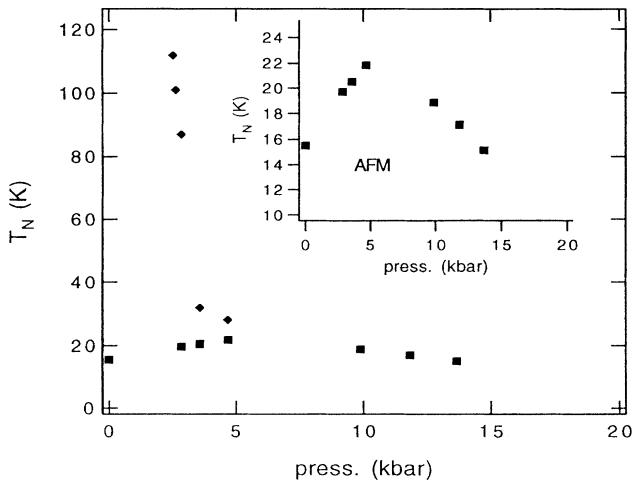

FIG. 2. Temperature for magnetic order T_N (squares) vs pressure phase diagram for $(TMTTF)_2Br$ illustrating the connection of T_N^{max} to the minimum in resistivity T_ρ (diamonds).

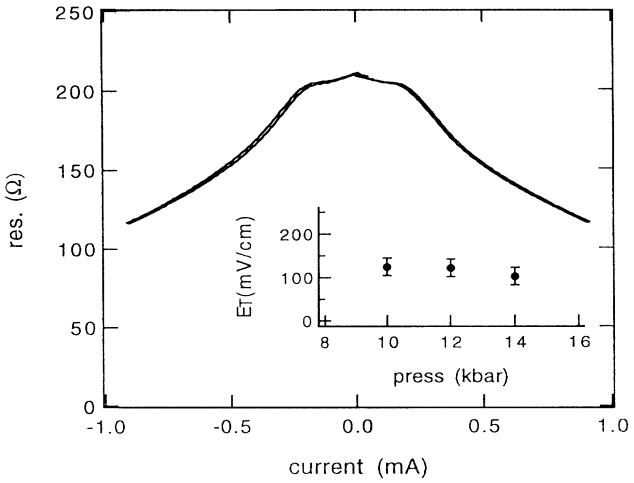

FIG. 3. Differential resistance vs current for a $(TMTTF)_2Br$ sample at approximately 13 kbar showing a clear threshold current I_T beyond which the transport behavior is strongly nonlinear. The inset shows that the threshold has no pressure dependence outside of experimental uncertainties.

a plane-wave incommensurate SDW, the threshold field E_T would result from coupling of the SDW to impurities. Undoubtedly, the samples studied here are not of the same high quality as typical Se-PF_6 or Se-ClO_4 crystals. In the three-dimensional weak-pinning model, the dependence on defect concentration c varies as c^2 [23], and thus a larger E_T for S-Br is appropriate [24]. Further evidence for a sliding SDW was the observation of a pulse-sign memory effect in all three "high-pressure" samples [25].

Other possibilities should be considered. In the same weak-pinning framework, an important parameter is the length scale over which phase coherence is lost, known as the Lee-Rice length [23]. Of course, a "stiffer" density wave is associated with a longer Lee-Rice length, and the stiffness comes from the dispersion of the electronic states near the Fermi level. Competition between the stiffness and the potential of randomly distributed impurities are among the factors determining E_T. It has already been discussed that pressure should lead to a more imperfect nesting situation, arising from a corresponding change in the dispersion. Huang and Maki [26] have considered the effect of imperfect nesting on E_T in the weak-pinning limit. Qualitatively, pressure should increase the density-wave stiffness, and hence lower E_T. The inset of Fig. 3, on the other hand, shows no measurable change of E_T over the range of 10–14 kbar.

The transport data have very clear implications. As the pressure is increased, the electrons are much more delocalized, indicating that the importance of the dimerization gap is reduced. When coupling to the dimerization potential is weak enough, the nonlinear conductance would suggest that the system has become incommensurate, motivating us to investigate with a microscopic probe for some evidence of this. On a special batch of samples prepared with TMTTF molecules containing ^{13}C at the bridging sites of the dimer, we have performed magnetic resonance experiments at 75 MHz and four different pressures: 1 bar, ~4 kbar, 8 kbar, and 13 kbar. In the salt, these two sites are inequivalent. The experiments were carried out using a Bruker MSL-400 spectrometer at Orsay.

For reasons of brevity, we show the line shape at low temperatures ($\sim \frac{1}{4}T_N$) for the extreme pressures, 1 bar and 13 kbar. At the least they are very different. While there are some differences in linewidth above the transition as the pressure is changed, these are small compared to the evolution below the transition.

The low-temperature line shape at 1 bar [Fig. 4(a)] is similar to that reported in Ref. [17], where it was offered as evidence for a CSDW. It is a very broad line on the order of 150 kHz (representing about 200 G for ^{13}C). Within the broad line are several sharp features. The significance is that there are large numbers of nuclei with the same local field, a hallmark of density wave commensurability with the lattice. In addition, there is a "hole" in the center of the line, indicating that there are few, if any, ^{13}C nuclei with the "average" local field.

On the other hand, the sinusoidal spin modulation of incommensurate systems leads to a broad continuum of local fields at the nuclei. This is reflected in the observed spectra of systems such as Se-PF_6 [16]. With our system, including two inequivalent carbon nuclei, incommensurability is expected to result in a full line shape that is a sum of two broad parts that are not necessarily of the same width. Based on the results shown in Fig. 4(b), we cannot say unequivocably that we observe the plane-wave incommensurate phase. However, it is clear that the hole in the spectral density at the center of the line is filled in, and the broad tails of the commensurate phase are practically unobservable. In a follow-up publication, we will present spin-lattice

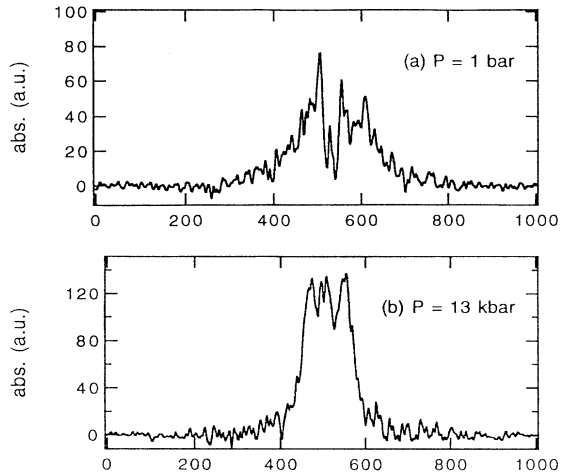

FIG. 4. ^{13}C line shape at a magnetic field corresponding to 75 MHz and $T \sim \frac{1}{4}T_N$. (a) $P = 1$ bar, (b) $P = 13$ kbar.

relaxation data which support the contention that the high-pressure phase is incommensurate [27]. The line-shape data at 8 kbar are similar to the data of 13 kbar, and the line-shape data of 4 kbar are similar to the 1 bar data.

This leads us back to the phase diagram of Fig. 2. As we noted, the ordering temperature $T_N(P)$ is shown as well as the minimum in the resistivity, T_ρ. From this figure, the nonlinear transport, and the ^{13}C NMR line shape it is apparent that several features distinguish the low-pressure regime from the high-pressure regime. First, a change of sign of dT_N/dP divides the two; as we have noted, we do not know if T_N is singular at $P_M \sim 5$ kbar. Although a very sharp crossover is more likely, this question will be investigated in upcoming experiments. Second, only at pressures above P_M do we observe the pulse-sign memory and distinct threshold electric fields. Third, at select pressures within the two regimes, the NMR line shape appears either to be characteristic of commensurate SDW's (low pressures) or consistent with an incommensurate line shape (high pressures). Finally, all of these crossovers in the behavior are identified closely with the pressure, where T_ρ approaches T_N. We consider the set of these observations to be good evidence that the same microscopic physics which leads to the charge gap drives the system to a commensurate, local-moment, antiferromagnetic state. At low pressures and $T < T_\rho$, the existence of the charge gap suppresses any single-particle transverse tunneling. The spin degrees of freedom on neighboring chains could couple via particle-hole tunneling processes, which stabilizes the antiferromagnetic phase [28,29]. In this regime, pressure has the effect of *increasing* this coupling, thus leading to a higher T_N. When the charge gap becomes unimportant (i.e., smaller than T_N), the ground state is similar to $(TMTSF)_2PF_6$, which is to say that the itinerant antiferromagnetism arises from repulsive electron-electron interactions and a slightly imperfectly nested Fermi surface. The result is an incommensurate spin-density wave forming at low temperatures with a transition temperature decreasing with pressure as the nesting is worsened.

We do not know whether the transition between the two states is of the first order and occurs when the charge gap becomes less than T_N, or whether there is a crossover or higher-order transition. Another possibility was suggested by MacMillan for CDW's in 2H-$TaSe_2$ [30]. In that system, there is a normal metal–incommensurate transition near 120 K, and 89 K the wave vector locks in at a commensurate value. Between the two transition points, a discommensuration lattice forms, with the density of the discommensurations tending toward zero at the lock-in transition.

The possibility for the occurrence of a similar scenario in the Bechgaard salts would be very interesting. Indeed, the pressure dependence of the properties of $(TMTTF)_2Br$ should be explored further to check whether there are charged discommensurations and if they respond to electric fields.

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[1] D. Jerome, in *Organic Conductors: Fundamental and Applications,* edited by J. Farges (Marcel Dekker, Inc., New York, 1994), p. 405.
[2] D. Jerome and H. J. Shulz, Adv. Phys. **31**, 299 (1982).
[3] G. Montamboux, Physica (Amsterdam) **177B**, 339 (1992).
[4] S. S. P. Parkin *et al.,* Phys. Rev. B **26**, 6319 (1982), and references therein.
[5] F. Creuzet *et al.,* J. Phys. (Paris), Lett. **43**, L755 (1982).
[6] K. Mortensen *et al.,* Phys. Rev. Lett. **46**, 1234 (1981).
[7] D. Jerome *et al.,* J. Phys. (Paris), Lett. **41**, L95 (1980).
[8] Coulon *et al.,* J. Phys. (Paris) **43**, 1059 (1982).
[9] S. Flandrois, C. Coulon, and P. Delhaes, Mol. Cryst. Liq. Cryst. **79**, 307 (1982).
[10] A. Maaroufi *et al.,* Mol. Cryst. Liq. Cryst. **119**, 311 (1985).
[11] J. P. Pouget, R. Moret, and R. Comes, Mol. Cryst. Liq. Cryst. **79**, 129 (1982).
[12] S. Baristic and Brazovski, in *Recent Developments in Condensed Matter Physics,* edited by J. Deversee (Plenum, New York, 1981), Vol. 1, p. 317.
[13] V. J. Emery, R. Bruinsma, and S. Barisic, Phys. Rev. Lett. **48**, 1039 (1982).
[14] See, for example, C. Bourbonnais, in *Low Dimensional Conductors and Superconductors,* edited by D. Jerome and L. G. Caron, NATO ASI Series B, Vol. 155 (Plenum, New York, 1987), p. 155, and references therein.
[15] T. Takahashi *et al.,* J. Phys. Soc. Jpn. **55**, 1364 (1986).
[16] J. M. Delrieu *et al.,* J. Phys. (Paris) **47**, 839 (1986).
[17] E. Barthel *et al.,* Europhys. Lett. **21**, 87 (1993).
[18] P. Wzietek *et al.,* Synth. Met. **55-57**, 2803 (1993).
[19] S. S. P. Parkin *et al.,* J. Phys. (Paris) **44**, 975 (1983).
[20] L. Balicas *et al.,* J. Phys. I (France) **4**, 1539 (1994).
[21] G. Montambaux, in *Low Dimensional Conductors and Superconductors* (Ref. [14]), p. 233.
[22] Conductivity nonlinearities have been reported by S. Tomic *et al.* [Europhys. Lett. **26**, 295 (1994)] at 1 bar and much larger electric fields. The relationship of these observations to those reported here is not yet known.
[23] P. A. Lee and T. M. Rice, Phys. Rev. B **19**, 3970 (1979).
[24] W. Kang, S. Tomic, and D. Jerome, Phys. Rev. B **43**, 1264 (1991).
[25] B. J. Klemme *et al.* (unpublished).
[26] X. Huang and K. Maki, Phys. Rev. B **42**, 6498 (1990).
[27] P. Wzietek *et al.* (unpublished).
[28] C. Bourbonnais and L. G. Caron, Europhys. Lett. **5**, 209 (1988).
[29] C. Bourbonnais, in *Proceedings of the International School of Physics, "Enrico Fermi,"* Course No. 106, *"Antiferromagnetism and Superconductivity in Organic Conductors,"* edited by G. Chiarotti, F. Fumi, and M. P. Tosi (North-Holland, Amsterdam, 1988).
[30] W. L. McMillan, Phys. Rev. B **14**, 1496 (1976).