Spin waves, scattering at $4k_F$, and spin-Peierls fluctuations in an organic metal: tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ)

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An interpretation is given for recent diffuse x-ray and neutron scattering experiments on tetrathiafulvalene-tetracyanoquinodimethane using a model of strong Coulomb interactions. The diffuse x-ray scattering observed at $q = 0.59b^*$ ($4k_F$) is identified as quasielastic scattering from a charge-density wave which is driven by long-range Coulomb interactions, while the scattering at $q = 0.295b^*$ ($2k_F$) is due to a Kohn anomaly caused by spin-Peierls fluctuations. Three experiments are proposed in order to verify this interpretation, including a search for spin waves which are predicted to be observable by inelastic neutron scattering near $q = 0.295b^*$.

I. INTRODUCTION

Recent diffuse x-ray experiments[1-3] as well as neutron scattering measurements[1,4,5] are providing information on the organic metal tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) which is far more direct and definitive than previous bulk measurements. In this paper, we shall concentrate on the temperature range above the phase transitions (i.e., $T > 53$ K) and examine the three different regions where experiments have been performed: (a) the region near $q = 4k_F$, where x-ray diffuse scattering was discovered by Pouget *et al.* and Khanna *et al.*,[2] and by Kagoshima *et al.*[3]; (b) the region near $q = 2k_F$ at energies above and below the TA-phonon branch which has been explored by inelastic neutron scattering by Mook and Watson at Oak Ridge[4]; and finally (c) the TA-phonon mode itself, which softens near $2k_F$, as discovered by Shirane *et al.* at Brookhaven[5] and also observed in diffuse x-ray scattering.[1-3] We propose[6,7] that the scattering in these regions will be dominated by, respectively: (a) a charge-density wave driven by long-range Coulomb interactions, (b) the direct excitation of spin waves, and (c) a Kohn anomaly associated with spin-Peierls fluctuations (as opposed to the usual electronic Peierls fluctuations).

We shall start by considering the simplest theoretical model of TTF-TCNQ which demonstrates these effects. This is the Hubbard model in the limit where the bandwidth $4t$ is less than the Coulomb repulsion energy U between two electrons on the same molecule. In this limit, the excitation spectrum of a one-dimensional stack with ρ electrons per molecule has been calculated by Coll[8] for $\rho < 1$ and is shown in Fig. 1. As in the familiar case[9] of $\rho = 1$ (the "half-filled band"), there are separate spin-wave and electron-hole excitations. But unlike the insulating $\rho = 1$ case, which has a large Mott-Hubbard energy gap in the electron-hole excitations,[9] there is no such gap in the $\rho < 1$ case,[8] and hence such materials can be highly conducting even if $U \gg 4t$.

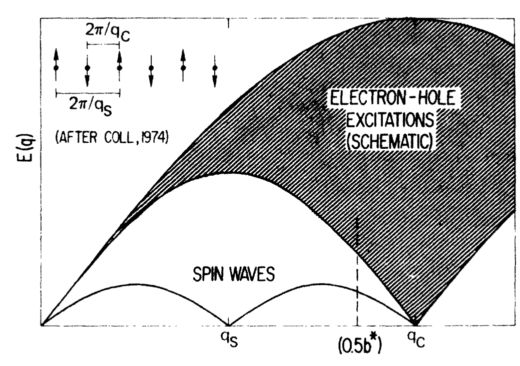

FIG. 1. Calculated excitation spectrum of the Hubbard model with strong correlations showing the spin-wave and electron-hole excitations.

II. SCATTERING AT $4k_F$

The x-ray experiments on TTF-TCNQ initially revealed[1] diffuse scattering at $q = 0.295b^*$ (b^* is the reciprocal-lattice vector in the b direction) which was called $2k_F$. Very recently, additional scattering has been discovered[2,3] at $q = 0.59b^*$, i.e., at twice the wave vector observed initially, or "$4k_F$". We suggest[6,7,10] that the latter anomalous scattering is associated with the wave vector $q_c = \rho b^*$ characteristic[7,8,11] of charges in the presence of *strong* Coulomb interactions. There are two possible origins[7] of the observed scattering at $q_c = 0.59b^*$: (a) a phonon softening (Kohn anomaly) caused by Peierls-like fluctuations, which remove the degeneracy at q_c in the excitation spectrum of Fig. 1 [note that in this case,[8,11] $2k_F = q_c$

is twice the usual ($U=0$) Peierls wave vector] or (b) (as we believe[7,10]) a charge-density wave (CDW) driven by long-range Coulomb interactions, i.e., a Wigner-like crystal, as predicted in Refs. 10 and 12. Such an ordered lattice of charges could be observed by x rays and neutrons through the strong electron-phonon coupling,[13] for example.

There is a qualitative difference in the driving energy for these two possibilities: in the case of a Kohn anomaly, the energy gained is kinetic (or band) energy, while Coulomb energy is gained by the formation of the Wigner-like crystal (CDW). Experimentally, these two alternatives may in principal be distinguished by inelastic neutron scattering near $q=0.59b^*$: a Kohn anomaly would be manifested as a phonon softening, while the Coulombically driven CDW, which we suggest,[7] would be observed as mostly quasielastic scattering. This distinction might be less clear if the Kohn anomaly were already condensed at the highest measurable temperatures. Nevertheless, it would be an important experiment to determine by neutron scattering whether the $4k_F$ scattering observed by x rays is quasielastic or arises from a deepening Kohn anomaly.

Recently, Emery[14] has interpreted the scattering at $4k_F$ as a Kohn anomaly similar to that discussed above, but described as a correlated state of *a number* of CDW. The observed wave vector ($q=0.59b^*$) is then regarded as *twice* the characteristic wave vector of the electronic system, or $4k_F$. In both of the cases discussed above, the scattering wave vector is viewed as *equal* to the characteristic wave vector $q=q_c=\rho b^*$ of the charges, or $2k_F$ Nevertheless, each of these three interpretations involves strong, or at least intermediate, Coulomb correlations (in fact, Emery[14] obtains[7] $U/4t>2$) and the same value of $\rho=0.59$.

III. SPIN WAVES

In the one-dimensional model, there is an antiferromagnetic exchange interaction J between spins, which causes the wave vector q_s of the spin system to be half as large as that, q_c, of the charges, as seen at both the top and bottom of Fig. 1. This interaction between spins gives rise to the spin-wave dispersion relation[8] (Fig. 1):

$$E(q)=\pi J\left|\sin(2\pi/\rho)(q/b^*)\right| . \qquad (1)$$

For $\rho=1$, Eq. (1) reduces to the familiar des Cloizeaux–Pearson[15] dispersion relation, with $J=2t^2/U$. With $\rho=0.59$ (as in TTF-TCNQ) the spin-wave energies are determined[16] by Eq. (1) with[8] $J=1.3t^2/U$. From an analysis[17] of the magnetic susceptibility, we infer a value of $J\sim 180$ °K.

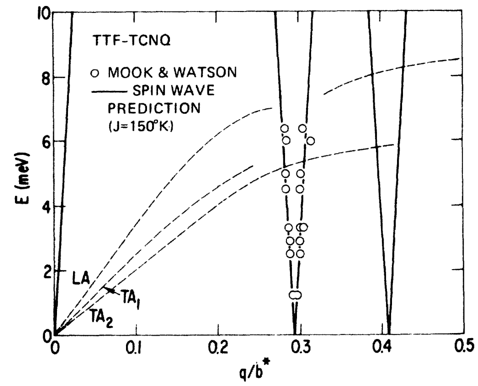

FIG. 2. Predicted spin-wave dispersion (solid lines) along with the scattering published by Mook and Watson (open circles), which has been recently questioned.

Using $J=150$ °K, the predicted spin wave $E(q)$ is shown in Fig. 2, where we have blown up (50×) the low-energy region of Fig. 1 in order to have it on the same scale as the experiments. The excitations are "folded back" across the crystal zone boundary at $q=0.5b^*$, so that the excitations near $q=0.59b^*$ are at the equivalent position $q=0.41b^*$. (For simplicity, the charge excitations near $q=0$ and $0.41b^*$ are not shown in Fig. 2.) Thus, we would expect to be able to observe the direct excitation of these spin waves (Fig. 2) by inelastic neutron scattering, as has been found in more conventional ($\rho=1$) quasi-one-dimensional systems.[18] Note that the scattering intensity in these latter systems is expected and is observed[18] to be much stronger near q_s ($=2k_F$) than near $q=0$ or $2q_s$. In an x-ray experiment, on the other hand, no scattering would be observed since x rays do not have spin.

A second type of scattering possible in this region has been suggested by Carneiro[19]: a giant Kohn anomaly involving optical phonons. There are, however, a number of reasons why such an anomaly is not present in TTF-TCNQ at 300 °K, as suggested[19]: (a) the magnitude of the magnetic susceptibility is sufficiently large[17] to rule out a very soft phonon near $q=0.295b^*=2k_F$ and (b) the particular phonon proposed (one involving the hydrogen atoms) is not expected[13] to couple strongly to the electronic system. (This particular phonon was suggested because the hydrogens would scatter x rays only very weakly, and hence the proposed giant Kohn anomaly would not be (and has not been) observed in x-ray scattering experiments).

For historical purposes, we also show in Fig. 2 the 300 °K inelastic neutron data previously published by Mook and Watson[4] (open circles). This weak scattering near $q=0.295b^*$ (the second region) was initially viewed[4] as a giant Kohn anomaly in the LA branch and has been subsequently interpreted as spin-wave scattering[6,7] and as a giant Kohn anomaly in an optical-phonon branch.[19] Considerable attention and controversy has centered on the data of Fig. 2, because of their dramatic dispersion relation, because of the suggestion that they are associated with spin waves or Kohn anomalies, and because of concern over their weak scattering intensity. Although additional scans made at Oak Ridge[20] at energies *above* the LA-phonon branch might suggest spin waves, the scattering intensity is not stronger than the very weak scans of Ref. 4. Very recently, several of these scans have been repeated in a series of joint experiments[21] at Brookhaven and Oak Ridge. It was concluded[21] that the scattering near $q = 0.295b^*$ in Fig. 2 is sufficiently weak at 300 °K, that no distinct anomalies could be observed. Therefore, *we must regard spin waves in* TTF-TCNQ *as a prediction*, which must await further, more conclusive neutron experiments in order to be verified.

IV. SPIN-PEIERLS FLUCTUATIONS

We now turn to the third region of study of these experiments—the softening of the TA phonon near $q = 0.295b^*$ (or $2k_F$). In Fig. 3 we show the temperature dependence of the diffuse x-ray scattering intensities observed[2] at the two wave vectors. The strong temperature dependence of that at $q = 0.295b^*$ and its transverse polarization are similar to those of the Kohn anomaly in the TA branch discovered by Shirane *et al.*,[5] demonstrating[1-3,5] that both of these techniques are measuring the same Kohn anomaly. Concerning the origin of this anomaly, the most direct interpretation is that it is associated with the CDW instability still present[14] at $2k_F$ for intermediate $U/4t$. We note also that a libron[22] or a *transverse* phonon might soften at $q = 0.295b^*$, since it would modulate the transfer integral at $q = 0.59b^*$. In the case of strong

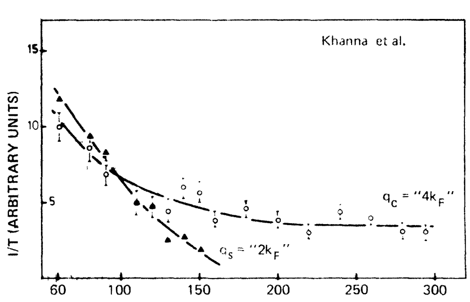

FIG. 3. Temperature dependence of the intensity of x-ray diffuse scattering at both wave vectors (after Khanna *et al.*, Ref. 2).

Coulomb interactions, there is a third possibility: note in Fig. 1 that a phonon with wave vector $2k_F$ or q_s can strongly effect only the spin system. Hence, we suggest[7] that the Kohn anomaly at $q = 0.295b^*$ is associated with spin-Peierls fluctuations, in which phonons remove the spin-wave degeneracy at q_s. (To be more precise, the phonons remove the degeneracy at q_s of the *two*-spin-wave continuum.) This suggestion involves a generalization of the spin-Peierls effect[23,24] from the Heisenberg linear chain ($\rho = 1$) to the case of $\rho < 1$.

For $\rho = 1$, the spin-Peierls instability and some of its unique features are most easily viewed by transforming the spins of the Heisenberg Hamiltonian into a half-filled band of pseudofermions.[25] If the interaction terms are treated in the Hartree-Fock approximation,[24,26] this band of pseudofermions is formally identical to a half-filled tight-binding electron band. The spin-Peierls instability may then be viewed[24] as a Peierls instability in the pseudofermion band, which will lead to a dimerization of the stack and the opening of a gap at the Fermi energy. The case of $\rho < 1$ can also be represented[27] by a half-filled band but with the wave vectors scaled by ρ so that the spin-Peierls instability would occur at $q = \rho b^*/2 = 2k_F$. The effect of a magnetic field on this system is to decrease the Fermi energy,[25,26] which has two consequences: (a) there is a decrease in the number of pseudofermions, which corresponds to a decrease in the number of down spins, and hence a net magnetization is induced by the field; and (b) the Fermi wave vector is shifted[24] (decreased) by the presence of the magnetic field. From the work of Pytte,[24] this shift is readily calculated to be:

$$2k_F(H) - 2k_F(H=0) = -2k_F(H=0)\frac{2\mu_B H}{(4+\pi)J} . \qquad (2)$$

For TTF-TCNQ with $J = 150$ °K, an external field $H = 100$ kOe, for example, is predicted to decrease the wave vector from $q = 0.295b^*$ to $0.291b^*$. Thus, we would predict that the Kohn anomaly in the TA phonon at $q = 0.295b^*$ (which we interpret as spin-Kohn anomaly) should shift with a magnetic field. An experimental search for this shift would help answer the important issue of whether the Kohn anomaly at $2k_F$ (and hence the phase transitions) is associated with the spin or charge excitations.

It is important to examine these effects in the presence of strong spin-Peierls fluctuations. As discussed above, an applied magnetic field decreases both the Fermi energy and the Fermi wave vector of the pseudofermions. As the temperature is lowered, spin-Peierls fluctuations (at the decreased wave vector) are expected to grow in magnitude. Since the Fermi energy has already been decreased by the magnetic field, there is an appreciable magnetization (i.e., susceptibility), even if the fluctuations are very strong.[28] In contrast, for the case of usual electronic Peierls fluctuations, the susceptibility is exponentially small. In TTF-TCNQ just above the phase transitions ($T > 60$ °K), where the fluctuations might be very large, the susceptibility does not decrease toward zero. In this sense, it behaves more as if the fluctuations were spin Peierls in origin. In fact, we interpret the anomalous decrease in the susceptibility below 300 °K as due to increasing fluctuations at $q = 2k_F$, which are spin-Peierls fluctuations and hence do not decrease χ as rapidly as usual Peierls fluctuations would. Similarly, increased intensity of spin-Peierls fluctuations are also invoked to account for the dramatic decrease of χ with pressure,[29] and the decrease in the donor χ in going from TTF-TCNQ to tetraselenafulvalene-TCNQ (TSeF-TCNQ) to hexamethylene-TSeF-TCNQ (HMTSeF-TCNQ). The increased intensity of spin-Peierls fluctuations proposed for the latter two compounds appears to be supported by the increased intensity and coherence length of the measured x-ray diffuse scattering.[30]

V. SUMMARY

In conclusion, we have applied a model with strong Coulomb interactions to interpret and understand the major features of the x-ray and neutron experiments on TTF-TCNQ, which are summarized in Fig. 3. The presence of scattering at two wave vectors is interpreted as due to distinct charge and spin excitations which have separate characteristic wave vectors q_c and q_s, with $q_c = 2q_s$. The diffuse x-ray scattering observed at $q = q_c = 0.59b^*$ (or $2k_F$) is identified as arising from quasielastic scattering from a CDW which is driven by long-range Coulomb interactions. Since these interactions are assumed stronger than kT, the intensity is expected to be large at all temperatures (as seen in Fig. 3). On the other hand, the scattering at $q = 0.295b^*$ (or $2k_F$) is identified as associated with the spin system q_s, and hence has a characteristic scale temperature of $J \sim 150$ °K. Thus, the scattering is expected to become appreciable for $T \sim J$ and rise sharply for lower temperatures as the antiferromagnetic correlations grow. This qualitative behavior is just what is observed (Fig. 3). Thus, the x-ray and neutron scattering provide further indications of the importance of Coulomb interactions[7] in the organic metal TTF-TCNQ.

We also note that recently these ideas[7] have been extended to other TCNQ salts by Sumi.[31] Also, Hubbard[32] and Kondo and Yamaji[33] have considered the Wigner-like crystal in the limit $4t = 0$ and have found important, additional effects which were neglected here and in Ref. 7. It has been asserted[34] that spin-Peierls transitions also are present in alkali-metal TCNQ salts. In addition, x-ray diffuse scattering has been reported at room temperature in N-methylphenazyl-TCNQ (NMP-TCNQ) by Ukei and Shirotani.[35] The fact that these authors observe up to five harmonics is strong evidence that the scattering in NMP-TCNQ is due to a Coulombic CDW, and not a Kohn anomaly. Very recent inelastic neutron scattering experiments[36] on the LA phonon mode in TTF-TCNQ at 300 °K have failed to reveal an anomaly near $4k_F$.

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