1:1 Alkali-TCNQ Salts and the Bond Order Wave (BOW) Phase of Half-filled Linear Hubbard-type Models

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The neutral-ionic transition (NIT) in organic donor-acceptor crystals is driven by Coulomb interactions. The NIT resembles the charge density wave (CDW) transition at $V > U/2$ of the half-filled extended Hubbard model (EHM) in 1D with on-site repulsion $U > 0$ and nearest-neighbor V. The bond order wave (BOW) phase of the EHM and related models with Coulomb interactions is close to the CDW boundary and requires sufficiently large transfer integral t for a continuous CDW transition. The narrow BOW phase is poorly characterized aside from broken inversion symmetry in a regular array of sites, a long range BOW and a finite energy gap E_m to the lowest triplet excited state. The 1:1 salts of TCNQ with M = Na, K, Rb or Cs are all close to the CDW boundary [1]. The Na and K salts dimerize below $T_d > 300$ K, while the polymorph Rb-TCNQ(II) retains regular stacks down to 100 K [2]. Evidence is presented that Rb(II) is the first realization of a BOW system: It has 1D stacks of $TCNQ^-$ anion radicals at inversion centers, negligible spin susceptibility below 150 K indicating finite E_m, and polarized mid-infrared spectra that signify broken electronic inversion symmetry. The BOW amplitude in Rb-TCNQ(II) is somewhat smaller than in dimerized systems (K or Na or Rb(I)) and has a strikingly different, cooperative T dependence. The absolute spin susceptibility, $\chi_M(T)$, increases nearly linearly for $T > T_d$ in Na or K-TCNQ and for $T > 230$ K for Rb(II), quite unlike what has been calculated in Hubbard-type models. To demonstrate quasi-linear $\chi_M(T)$ in a model system, we studied the BOW phase of a linear Heisenberg antiferromagnet with frustrated first and second-neighbor exchange and a well known fluid-dimer transition at 0 K. The wide BOW phase of the spin chain is clearly seen and well converged in finite systems with periodic boundary conditions. Finite E_m leads to quasi-linear $\chi_M(T)$ and a broad, almost constant maximum that corresponds to a uniform density of singlet-triplet systems. The double degeneracy of the BOW ground state raises interesting open questions for linear electron-phonon or spin-phonon coupling and for the Peierls instability to dimerization.

[1] M. Kumar *et al.*, Eur. Phys. Lett. 83 (2008) 37001.
[2] T. McQueen *et al*. Chem. Phys. Lett. 475 (2009) 44.