Charge ordered state and its stabilization in organic compounds

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ABSTRACT

With 1D and 2D organic compounds as examples, it is shown that for stabilization of the charge ordered state the appropriate reorganization of anion and molecular sublattices is necessary.

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Studies show that at a certain temperature the homogeneous distribution of charge along molecular chains changes by the appearance of charge-rich and charge-poor molecules. The formation of the CD with decreasing temperature was confirmed by X-ray diffraction patterns corresponding to a $4k_F$ charge density modulation of the Wigner crystal type.

The studies of real and imaginary parts of $\chi''$ in other quasi-1D organic compounds of the (TMTTF)$_2$X family (where X are anions of various charge symmetry) show the characteristic features indicating a second-order phase transition near some temperature $T_C$, into a new CO ground state: sharp decrease of the conductance and divergence of the dielectric permittivity $\varepsilon'$ in accordance with the Curie law [2,3]. These results were confirmed by NMR studies in (TMTTF)$_2$X which show the splitting of NMR lines at $T < T_C$ corresponding to the formation of CD along TMTTF chains [5]. At the same time, X-ray studies of these compounds do not bring any indication of changes in the molecular lattice at the transition into the CO state, which was called "structureless transition" [6].

However, in spite of the unit cell of the molecular lattice is not changed, the space symmetry is changed as a result of the lost of the inversion centre [2,3,7]. For compensation of such changes, it was proposed [2,3,7] that the shift of the anion chains as a whole with the wave vector $q = 0$ turns out to be the most advantageous. That leads to the removal of the charge symmetry disbalance and the restoration of the stability of the molecular crystal. Thus, the stabilization of the CO state occurs by the shift of the anion chains with respect to their initial symmetrical positions.

3. Stabilization of CO in 2D organic compounds

The experimental evidence of the formation of CO in the 2D organic compound $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$ (RbZn salt) was...
obtained first by NMR studies [8]. Considerable changes in the NMR line shape were found below $T_{CO} = 200\,\text{K}$ resulting from charge-rich and charge-poor sites. Raman spectroscopy on RbZn salt has shown a splitting of the charge sensitive C==C stretching mode indicating a charge difference among the ET molecules [9]. The character of the state developed at $T < T_{CO}$ depends on the cooling rate.

We have carried out measurements of the conductance $G$ and the dielectric permittivity $\varepsilon'$ in RbZn salt in 4.2–300 K and $10^{3}$–$10^{7}\,\text{Hz}$ ranges [10]. It was found that at slow cooling (0.1–0.2 K/min) $\varepsilon'$ begins to grow already from room temperature (Fig. 1). Near $T_{CO}$ $\varepsilon'(T)$ shows a sharp, close to a divergence, growth in a narrow temperature interval. A jump-like decrease of $\varepsilon'$ occurs just below $T_{CO}$. On heating, the jump up of $\varepsilon'$ is observed at about 3 K $T_{CO}$. The character of the $G(T)$ and $\varepsilon'(T)$ dependences is typical for a first-order transition.

The monotonic increase of $\varepsilon'$ with cooling from room temperature to the vicinity of $T_{CO}$ can be associated with short-range charge inhomogeneities as detected by the broadening of the NMR spectra or the observation of diffuse planes and rods with $q = (q_{1},q_{2})$ [11]. The $\varepsilon'$ peak developed near $T_{CO}$ resembles the one measured at the CO transition in (TMTTP)$_{2}$X salts [2]. At the CO transition in RbZn the diffuse rod with such $q$ disappears, the space group changes from orthorhombic $I222_{1}$ to $P2_{1}2_{1}2_{1}$, and the breaking of the inversion centre occurs [11]. The sharp decrease of $\varepsilon'$ below $T_{CO}$ is associated with the formation of the lattice superstructure $c'/2$ and with the opening of a large energy gap resulting in the decrease of the electron concentration by three orders of magnitude (Fig. 2).

As was mentioned above, the stabilization of the CO state in 1D Fabre salts occurs through the shift of the anion chains. In the case of RbZn salt, the CO stabilization is due to the formation of the lattice superstructure with a doubling period along $c$-axis. It can be associated with the relatively smaller mobility of the anions within the more rigid 2D lattice and with stronger electron-phonon interactions in the lattice compared to 1D compounds. Additionally, the development of the 2c superstructure leads to a decrease of the free energy of the system [12]. Thus, the development of the 2c superstructure is the consequence of the formation of the CO state, initiated by correlated interactions in the electron system and provides the possibility of the formation of the stable 3D CO state with large enough coherence length.

However, for fast cooling ($9–10\,\text{K/min}$) the low temperature state $\varepsilon'$ RbZn salt differs considerably from the appropriate state on slow cooling [13]. Fig. 2 shows the temperature dependence of the conductance of the RbZn salt for three cooling rates. The magnitude of the sharp drop, corresponding to the first-order transition, is decreased with increasing the cooling rate. For fast cooling the drop is practically suppressed and the activation energy below $T_{CO}$ decreases considerably.

Fig. 1 shows the dielectric permittivity $\varepsilon'$, normalized by its room temperature value $\varepsilon'_{0}$, as a function of temperature for the three cooling rates. At the intermediate cooling rate the maximum of $\varepsilon'$ decreases, shifts to lower temperature ($175\,\text{K}$) and becomes more wider in comparison with slow cooling. For the fast cooling there is no sign of any sharp divergence of $\varepsilon'$. Instead of that, $\varepsilon'(T)$ shows a very broad maximum around 150–200 K. On heating after intermediate and fast cooling we observed $t$ in the range 150–160 K the destabilization of quenched metastable states and the restoration to the $\varepsilon'(T)$ dependence analogous to the slow cooling.

We consider that the main reason of these transformations is the behavior of the molecular lattice at the fast cooling. The attempts of the electron subsystem to form the stable CO state meet the obstacle which lies in the fact that the lattice has not enough time to be coherently reconstructed on long enough lengths. As a result, parts of the sample with different degrees of transformation to the 2c superstructure and with small coherence lengths are developed. At $T < T_{CO}$ the state of the fast cooled RbZn sample is some mixture of initial ($T > T_{CO}$) and turned into CO states. This mixed state has a metastable character and it is destroyed on heating above about $150\,\text{K}$. Such a qualitative picture is verified by X-ray studies at fast cooling [11]. In the quenched state the diffuse rods with $q_{1} = (0,k,0)$, observed previously at $T > T_{CO}$, become weaker but still exist below $T_{CO}$. Additionally, at $T < T_{CO}$ another diffuse rods with $q_{2} = (0,k,1)$ appear. The moduluation of $q_{2}$ type is disordered in the interlayer direction. After annealing, $q_{2}$ grows into the satellite reflections of $c'/2$. The tendency to the formation of CO, exhibited by the electron subsystem but not supported by the appropriate modifications in the molecular lattice, does not lead to the formation of a stable CO state at the fast cooling.

In order to make more clear the nature of this quenched state we can use the results of studies of the $\theta$-(ET)$_{2}$CeZn(SCN)$_{4}$

Fig. 1. Temperature dependence of $\varepsilon'$, normalized by its room temperature value $\varepsilon'_{0}$, for RbZn salt at three cooling rates: slow—0.1 K/min (a), intermediate—4 K/min (o) and fast—0–9 K/min (C).

Fig. 2. Temperature dependences of $G$, normalized by its value at room temperature $G_{0}$, for RbZn salt for the same three cooling rates as in Fig. 1. Inset shows these curves in detail near $T_{CO}$. The top curve (a) shows $G$/$G_{0}/(1000/T)$ dependence for CsZn salt.
compound which is similar to the RbZn salt (see Ref. [14] and references therein). Infrared reflectance and Raman spectra show that no optical gap is observed in the CsZn salt in all the temperature range down to 10 K [15]. NMR studies show that, as in the case of RbZn salt at $T > T_C$, a line broadening is observed in CsZn salt below about 180 K which is associated with the development of a partial CD. X-ray studies show that in CsZn salt, as well as in isostructural CsCo [16,17], in the range 300–120 K strong diffuse sheets are observed along $2\pi + \pi$ and $2\pi - \pi$ directions. Below 90 K 2D diffuse rods corresponding to $q_1 = (q_2, k, \pi)$ and $q_2 = (0, k, \pi)$ develop from the diffuse sheets. With further cooling the peak intensity of $q_2$ increases while the $q_1$ charge modulation is also retained. The correlation lengths of $q_1$ and $q_2$ ranges (domains) are not very large (50–70 Å) [16].

We undertook measurements of the conductance $G$ and the dielectric permittivity $\varepsilon'$ of CsZn salt in order to elucidate the main features of its low temperature state [14]. The temperature dependence of $G$ shows a maximum near 110 K with a following bend down with a small thermal hysteresis. The Arrhenius plot of $G$ below the maximum is not linear in the temperature range 100–4.2 K (Fig. 2). It means, probably, that no real energy gap develops in CsZn salt, although the average “energy gap” is considerably smaller than in RbZn salt. An appreciable decrease of $G$ is observed at $T < 20 K$. In the range 4.3–20 K the most accurate fit of the dependence of the ac conductance corresponds to the relation $G(T) \sim T^n$ with $n = 2.9$. This value of $n$ is very close to the case of the hopping conductivity with disorder, taking into account also the electron correlation effects for which $G \sim T^3$ [18].

The temperature dependence of $\varepsilon'$ is shown in Fig. 3. The magnitude of $\varepsilon'$ begins to grow from room temperature. Below 100 K $\varepsilon'(T)$ dependences show maxima at some temperature dependent on frequency $\omega$. With decreasing $\omega$, this maximum shifts to lower temperatures. Simultaneously, the maximum magnitude of $\varepsilon'$ increases. Such forms of $\varepsilon'(T, \omega)$ dependences are very similar to the known slowing down behavior which is characteristic for glasses.

Thus, as it follows from the abovementioned results, with decreasing temperature the CsZn salt does not achieve the stable 3D CO state but turns into a glass-like CO state [14,19]. At low $T$ the existence of two types of domains with different structures, competing to each other, leads to the development of frustration, i.e. when incompatible and competing two fold ($q_2$) and three fold ($q_1$) states correspond to two degenerate free energy minima with very close values in their energy. As a result of such a frustration some glassy-like CO state develops; it corresponds to freeze some degree of disorder on the long-range scale but with conservation of the short-range order with a small coherence length [19].

4. Conclusion

For the stabilization of a CO state in 1D and 2D organic compounds, owing to electron-electron correlated interactions, certain modifications are needed in anion and lattice subsystems. In 1D Fabre salts that is the shift of anion chains as a whole with $q = 0$. In 2D compounds, such as $\delta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$, the stabilization is realized by the development of a superstructure with double of the lattice period. If with decreasing temperature this dimerization is not realized on a long-range scale but, instead of that, a conglomerate of many domains with different structures turns out to be frozen, a glass-like CO state is developed, as observed in $\delta$-(BEDT-TTF)$_2$CsZn(SCN)$_4$.

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