Scientific session of the Division of General Physics and Astronomy, USSR Academy of Sciences (24 September 1975)

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A scientific session of the Division of General Physics and Astronomy was held on September 24, 1975 at the conference hall of the P. N. Lebedev Physics Institute. The following papers were delivered:

1. *I. F. Shchegolev*, Electronic Properties of Quasi-One-Dimensional Mettallic Systems in TCNQ Complexes.

2. *L. N. Bulaevskiĭ*, The Peierls Transition in Quasi-One-Dimensional Crystals.

We publish below the brief content of the second paper.

L. N. Bulaevskiĭ. *The Peierls Transition in Quasi-One-Dimensional Crystals.* We now know of rather many compounds with rather high conductivity at room temperature (100 Ω^{-1} cm^{-1} and higher) and strong anisotropy of the one-dimensional type (conductivity anisotropy of the order of 100 or more). These crystals include complexes of platinum-group transition metals of mixed valence (for example, $K_2Pt(CN)_4Br_{03}\cdot 3H_2O$, KCP for short), TCNQ salts, and crystals of $(SN)_x$ polymers. But all compounds of this type except $(SN)_x$ become dielectrics at low temperatures. It has been established by experiment that the metal-dielectric transition in KCP and TTF–TCNQ crystals is governed by Peierls instability, which is inherent to systems with one-dimensional or almost one-dimensional motion of conduction electrons.

The one-dimensional metallic system with rather weak Coulomb interaction of electrons is unstable under distortions of the lattice with period $1/2k_F$, where k_F is the Fermi momentum of the electrons. Within the framework of the self-consistent-field model, this distortion appears below the temperature T_p of the Peierls instability and results in splitting of the conduction band into fully populated and empty subbands with an energy gap between them. As the temperature T approaches T_p from above, a gap appears in the phonon spectrum at a quasimomentum $2k_F$ (giant Kohn anomaly), the frequency of these phonons vanishes at the point T_p itself, and Peierls distortions appear below T_p as a result of condensation of phonons with momentum $2k_F$.

Allowance for the fluctuations, which are significant for the one-dimensional system, and allowance for the interaction between the distortions of different chains in the crystal result in modification of this simplest of pictures of the Peierls transition if the interaction of the chains is sufficiently weak. In this situation, large regions with Peierls distortions appear within the chains near the temperature T_p, but there is no long-range order over the entire chain and no correlation between chains. At a temperature around $T_p/4$, long-range order has for all practical purposes been established along the chain, and correlations appear between the displacements in different chains.

The experimental data definitely indicate that precisely this picture of the Peierls transition is observed in KCP. X-ray and neutron scattering in KCP at temperatures above 120 °K have established the existence of correlations between the displacements of ions along the chains that correspond to tripling of the original period, while the displacements between chains become correlated below 120 °K. The existence of the giant Kohn anomaly in the phonon spectrum of KCP is also confirmed by room-temperature neutron inelastic scattering experiments. In TTF–TCNQ, long-range correlations of the molecular displacements within the chains occur in the range from 60 to 40 °K (they correspond to a superstructure with a period equal to 3.7 periods of the original lattice), and correlations of the displacements of different chains appear below 40 °K.

Self-consistent-field calculations indicate that there is a collective mode corresponding to oscillations of the displacements of the ions and of the electrons relative to the ions (a Fröhlich collective mode) in the Peierls-dielectric state. This mode is optically active, and its frequency is lower, the greater the difference between the superlattice and original-lattice constants. The Fröhlich collective mode is manifested in a sharp absorption peak at a low frequency (≈ 0.002 eV) at temperatures below 120 °K in KCP. It results in a large value of the dielectric constant of KCP (≈ 1000) at low temperatures.

It is also affirmed in several papers that the Fröhlich collective mode makes an additional contribution to dc conductivity above T_p (in the fluctuation regime), and that this contribution increases as the temperature approaches T_p. However, there are also papers that question the existence of this effect.

In experiments, conductivity in KCP decreases monotonically with decreasing temperature, but in TTF–TCNQ there is a conductivity peak at around 60 °K. For some of the crystals prepared by Heeger's group at the University of Pennsylvania, the conductivity exceeds $10^5 \Omega^{-1} cm^{-1}$ in the peak, and arguments involving the Fröhlich collective mode are advanced to explain this high conductivity. The peak conductivities of crystals made in other laboratories around the world do not exceed $2\times 10^4 \Omega^{-1} cm^{-1}$, and the conceptions of the single-electron conductivity mechanism are sufficient to explain the peak. Thus, the question as to the height of the conduction peak in TTF–TCNQ and its interpretation still remains unresolved.

As a rule, Peierls instability interferes with realization of the superconductive state in systems of the quasi-one-dimensional type. Therefore superconductivity can be obtained only in systems with chain interactions that are strong enough to suppress Peierls instability. $(SN)_x$ crystals are precisely such systems—they have the lowest electronic-property anisotropy among crystals of the quasi-one-dimensional type. It will apparently be possible to synthesize organic "metals" and superconductors only when ways are found to reduce the electronic-property anisotropy of highly conductive organic crystals.

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