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Unstable and elusive superconductors

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ABSTRACT

We briefly review earlier and report original experimental results in the context of metastable or possible superconducting materials. We show that applied electric field induces conducting state in Copper Chloride (CuCl) whose characteristics resemble behavior of sliding charge-density-wave(s) (CDW). We discuss whether the sliding CDW or collective transport of similar ordered charge phase(s) may account for the problem of "high-temperature superconductivity" observed in this and other materials, including Cadmium Sulfide (CdS), metal–ammonia solutions, polymers, amorphous carbon and tungsten oxides. We also discuss a local superconductivity that occurs at the surface of graphite and amorphous carbon under deposition of foreign atoms/molecules.

Contents

1. History and state of the art

Since the discovery in 1911 by Heike Kamerligh Onnes of the superconductivity (SC) in mercury (Hg) with the transition temperature $T_c = 4.2$ K, an empirical approach in searching for new superconductors with higher T_c is still most successful one.

In recent times, the most spectacular achievement of such approach was the discovery of high-temperature superconducting (HTS) cuprates [1], allowing to use a practical liquid nitrogen ($T = 77$ K) instead of expensive liquid helium ($T = 4.2$ K) to reach the superconducting state. So far, the highest $T_c = 135$ K at ambient pressure was achieved for copper mercury oxide $HgBa_2Ca_2Cu_3O_9$ [2] and T_c was raised up to 164 K under pressure of 30 GPa [3].

The discovery of HTS left little doubts among researchers that the superconductivity at room temperature RTS (better to say at normal leaving conditions) is achievable.

There were published many review articles on the progress in superconducting materials, and *routes to RTS*, see e.g. [4–7].

In the present contribution we briefly describe some earlier reports on potential high-T_c superconductors and present our experimental results that shed more light on this and related long-standing

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problems. We shall only concentrate on the results duplicated by at least one independent experimental group.

Looking back on the history of superconducting materials, one sees that discovery of novel superconductors is often associated with initial findings of traces of unstable (transient) superconductivity due to presence of a small amount of a novel superconducting phase embedded in the parent material.

1.1. Cuprate high-T_c superconductors

In the beginning of 1987, Chu and collaborators have observed superconducting activities up to ~96 K in mixed-phase La–Ba–Cu–O samples [8] that have been lost in one day because of the sample degradation. Later on, the famous superconducting $LaBa_2Cu_3O_y$ (La-123) phase with $T_c \geqslant 90$ K was identified.

Various experimental groups reported a metastable, i.e. vanishing with time, superconducting response in Y–Ba–Cu–O samples even at room temperature.

For instance, Munger and Smith measured reverse ac Josephson effect in polycrystalline $YBa_2Cu_3O_{7-\delta}$ up to 300 K [9] and they have concluded that the RTS is related to the sample inhomogeneity. Remarkably, after 25 years, reports on metastable RTS in cuprates continue to appear in the literature. In Ref. [10] a transient RTS superconductivity has been triggered by light in $YBa_2Cu_3O_{6+\delta}$, attributed to the light-induced enhancement of the Josephson inter-layer coupling. Before that, conclusions on the enhanced coupling between neighboring Cu (2) – O (2) bi-layers caused by photo-assisted oxygen ordering [11] was made [12]. Hence, thermally unstable structures may be behind of transient RTS in cuprates.

A strong enhancement of T_c, as compared to the equilibrium bulk value, resulting from the surface adsorption of nitrogen, oxygen, helium has been also demonstrated [13,14]. Then, desorption of foreign atoms/molecules during the thermal cycling would naturally account for the T_c reduction, and hence, the metastable superconductivity.

1.2. Elusive high-temperature superconductors

1.2.1. Copper chloride and cadmium sulfide

Before the cuprate era, experiments performed on Copper Chloride (CuCl) [15–22] and Cadmium Sulfide (CdS) [23–25] were a major hope related to high-temperature superconductivity.

In 1978, Brandt et al. [15] reported a transition to the almost ideal diamagnetic state in CuCl below $T_d \sim 170$ K, accompanied by the resistivity drop of several orders of magnitude, when the samples under a hydrostatic pressure of ~5 kbar were rapidly (~20 K/min) cooled/heated. The "super-diamagnetic" state appears to be metastable such that T_d has decreased gradually by a factor of ~3 after several thermal cycles in the temperature range 4.2 K < T < 350 K. However, at constant temperature, the anomalous state was stable for hours. The results revealed a jumpy behavior of ac susceptibility between "zero" and "super-diamagnetic" state values. Similar results were obtained in the temperature interval $\Delta T \sim 20$ K around $T \sim 240$ K at slightly different conditions but again only under a rapid sample warming [16,17]. It was proposed [16] that under applied pressure and rapid temperature variation, the reaction $2CuCl \rightarrow Cu + CuCl_2$ leads to formation of Cu–CuCl metal–insulator metastable interfaces responsible for the transient HTS. The assumption that Cu solely is responsible for the observed diamagnetism requires the copper resistivity far smaller than known values.

While the pressure-induced insulator–metal transition (IMT) in CuCl has been widely explored, a similar IMT induced by applied voltage (V) [18,19] is less known. Gentile [18] showed that the electric-field (~3 kV/cm) driven IMT in CuCl is accompanied by the formation of Cu filaments, and Divakar et al. [19] demonstrated that both applied pressure and electric field drive the IMT such that the critical (threshold) electric field E_{th} decreases with the pressure increase. Besides, it has been observed that the insulating state reappears removing the applied voltage. The recovery time depends on various factors, and it could be as long as 3 days when the conducting state kept for 48 h [19].

The almost ideal diamagnetism [20], as well as the low resistance state (LRS) [21] below ~240 K were also observed in CuCl films grown on high purity Si(111) substrates. DC magnetization M(H) measured with the SQUID magnetometer was found to be paramagnetic or diamagnetic when the magnetic field (H) applied parallel or perpendicular to the CuCl/Si interface, respectively [20]. Such anisotropy implies a two-dimensional (2D) character of the phenomenon related to either the sample surface or CuCl/Si interface [20]. The authors [20] optically detected islands of the size as large as ~0.1 mm that break with time on smaller domains and form a hexagonal array during tens of days. The observed domain structure was not affected by a small variation of magnetic field or temperature but it was sensitive to mechanical deformations.

We recall that Auger electron spectroscopy and low-energy ion scattering studies [22] proved that CuCl/Si (111) interface is thermodynamically unstable, viz. Cu forms the outermost layer of CuCl film implying the Si–Cl bonding at the interface. Hence, it is possible that similar to bulk CuCl, formation of Cu/CuCl interfaces is responsible for the observed superconducting-like behavior.

Similar to CuCl, pressure-quenched CdS containing Cl impurities (0.6–0.8 wt.%) has been found to demonstrate superconducting-like behavior at temperatures well above 77 K [23,24]. The samples were prepared under applied pressure $P > 40$ kbar that was released at rates >10^6 bar/s. The quenched "as-received" samples demonstrated 5 orders of magnitude lower resistance and superconducting-like magnetization hysteresis loops M(H) with nearly perfect Meissner portion. These properties depend crucially on the Cl contents as well as pressuring, thermal and magnetic history. The experiments revealed that the metastable diamagnetism decays as the electrical conductivity. In Ref. [25] X-ray diffraction and photo-acoustic measurements have been made on CdS as a function of chlorine doping. The results revealed the Cl-induced cubic to hexagonal transformation accompanied by the presence of soft lattice modes over a critical range of Cl impurities where the superconducting-like state takes place. Furthermore, authors of Ref. [25] developed a theoretical model suggesting the occurrence of Fröhlich-type superconductivity [26] in CdS. In the Fröhlich theory there is no electron–electron pairing but superconductivity may result from a freely sliding charge density waves (CDW). When sliding CDW travel around closed loops, strongly diamagnetic state accompanied by the resistance drop should take place.

1.2.2. Polypropylene polymers

It is instructive to compare results obtained on CuCl and that reported for oxidized atatic polypropylene (OAPP) polymers [27–29].

Thick (0.3–100 μm) insulating polypropylene films were deposited on Cu or In substrate and after some thermal cycling the apparent zero-resistance state below $T \sim 300$ K has appeared [27,28]. Similar to CuCl, OAPP demonstrate a strong metastable diamagnetism. The reported results revealed that the initial sate of OAPP is weakly diamagnetic. After the field cycling in the interval $0 < B < 0.2$ T, the samples were found to be paramagnetic, ferromagnetic or strongly diamagnetic, resembling the behavior of superconductors in a partially penetrated Meissner state [27,29]. The experiments repeatedly showed spontaneous transformations between ferromagnetic- (FM) and SC-like states at