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RECENT DEVELOPMENTS OF HOME RESEARCH ON HIGH-Tc SUPERCONDUCTIVITY AND COLOSSAL MAGNETORESISTANCE: AN ATTEMPTED SURVEY[1]

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Abstract. Bulgarian solid state physicists and chemists have missed no chances to joining the global scientific effort of unravelling remarkable properties of condensed matter: the high-temperature superconductivity and the colossal magnetoresistance. This paper surveys some of the good homework done so far in ten branches of related scientific and technological interest.

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1 Introduction

Fourteen years after the discovery of a high-temperature superconductivity (HTS) in layered oxocuprates, the thrilling phenomenon is not understood well in spite of a tremendeous scientific effort. Bulgarian scientists having shared a good deal, it is perhaps time to draw up a balance. Appealing to the reader, we apologize for any omission of contributions that should have been mentioned.

The recurring structural property of the broad HTS family of oxocuprates are the copper-oxygen planes [1]. They are believed to provide a quasi-two-dimensional space for the conduction of electric currents by electrons or holes in normal state. The conducting planes are separated by insulating layers, or by metal oxide layers and incomplete layers or chains. Contemporary science attributes the superconductive currents to pairs of normal state carriers else excitations which pair through the mediation of a boson field and Bose condense below T_c. The challenge is the critical temperature T_c incompatible with the pairing mechanism mediated by phonons.

[1]Dedicated to the memory of Professor Eugene Leyarovski, Founder of the low-temperature research in Bulgaria

Another group of materials attracting attention lately is the manganites exhibiting a colossal magnetoresistance (CMR) [2]. $La_{1-x}Sr_xMnO_3$ being an example, it undergoes a phase transition from ferroelectric conductor to paramagnetic insulator as the temperature is raised across T_N, with a change of several orders of magnitude in electric resistivity in a magnetic field. Mn^{3+} being a Jahn-Teller (JT) ion, the ferromagnetic to paramagnetic conversion is regarded as one from itinerant large JT polarons to immobile small JT polarons.

2 Material Synthesis

After HTS was discovered, many oxide materials were synthesized and investigated. These were aimed at increasing T_c and elucidating the HTS pairing mechanism. The search for higher T_c proceeded by making substitutions in known materials and by synthesizing novel ones. We summarize some recent results below.

A cadmium analogue of the mercury system with nominal composition $CdBa_2Ca_{1-x}Y_xCu_2O_y$ was synthesized. The $x = 0$ samples contain about 12 vol.% of the 1212 phase but are not superconducting. The $x = 0.3$ samples are superconducting at $T_{\rm on} = 103$ K. The EDX analysis of 18 microcrystals shows a broad cationic distribution of the different components. The observed broad superconducting transition is attributed to T_c's of different microcrystals [3]. A new Cd-containing superconductor with nominal composition of $Cd_{0,8}Ba_2(Y_{0,7}Ca_{0,4})Cu_{3,5}O_y$ and $T_c = 80$ K was synthesized and investigated. The obtained XRD pattern indicates that the dominating phase is an orthorhombic 123. The presence of Cd and Ca facilitated the 123 phase formation. The results of EDX analyses on SEM and TEM revealed that the Cd and Ca distribution was nonuniform. Both elements entered the 123 phase in most of the investigated samples to form a new Cd-Ba-Y-Ca-Cu-O superconducting compound [4,5].

The effect of Sn substitution in a new mercury-based superconductor with nominal composition $(Hg_{1-x}Sn_x)Ba_2Ca_2Cu_3O_y$ (0¡x¡0.5) was studied. At this stage of the investigation, the material was multiphasic with dominating superconducting phases up to $x = 0.3$. We established that Sn stimulated the formation of the Hg-1212 phase and enhanced the diamagnetic volume fraction but also the weak-link behavior. Together with the SEM-EDS analysis, the shift of some of the XRD peaks and the gradual decrease of T_c with the dopant content x suggest that the substitution is effective as some Sn is incorporated into the superconducting phases [6]. The effect of Sn-doping in $(Pb_{0.7}Sn_{0.3})Sr_2(Y_{0.6}Ca_{0.4})Cu_2O_y$ was also investigated. The result of XRD, ICP-AES and EDX on SEM analyses showed that the obtained material contained the 1212 phase. EDX analysis in different points showed that tin was present in most of the microcrystals but its distribution was nonuniform. The resistivity and susceptibility measurements denoted superconductivity at $T_c = 20$ K. The dependence of the resistence on a magnetic field showed about 20% magnetoresistance at 4.2 K coexisting with the superconducting state up to $H = 1$ kOe [7]. Single-phased samples were obtained from $(Pb_{0.55}Sn_{0.1})Sr_2(Y_{0.73}Ca_{0.36})Cu_{2.33}O_y$.

The properties of high-T_c superconductors are sensitive to synthesis and processing which affect their structural anisotropy, granularity and complex phase formation. High-T_c super-conductors of the YBCO family were produced by solid state reaction and melt-quenching techniques [8,9]. The influence of doped or substituted elements (Pt, Ag, Te, Pb) were investigated along with the technological routes of phase formation and superconductivity. An improvement was reported of material properties (T_c, J_c, chemical stability). Ag and Te additions improved the phase formation, mechanical strength, magnetization, ac losses and the obtaining of super-conducting composites. Pt doping led to $J_c \sim 1058$ A/cm^2 at voltage drop 5 μV/cm at 80 K.

Pt has originally been incorporated subject to considerable debate at Institute of Solid State Physics, Bulgarian Academy of Science (ISSP BAS) [10]. Pt is doped by firing samples or films on Pt foils or in Pt crucibles. Pt improves J_c of the 123 phase ($Y_1Ba_2Cu_3O_{7-\delta}$) while reducing T_c. Pt doping of the YBCO family affects the microstructural composition of insulating 211 phase ($Y_2Ba_1Cu_1O_5$) in melt processing. A likely Pt effect is inhibiting the growth of the 211 bulk phase resulting in the uniform dispersion of 211 precipitates in the 123 bulk improving links at the grain boundaries.

2.1 Ceramics

Most investigations have been made on ceramic samples of the YBCO family by the Superconductivity Group at ISSP BAS under Professor V. Kovachev. Apart from a rich structure, what attracted the scientific interest might have been the relative ease of producing the samples. An example of good ceramics paper, the microstructure and phase formation of Nd-Ba-Cu-Ag-O ceramics is reported. Ag addition to YBCO ceramics stabilizes its super-conductivity. Only a small Ag content is found in the crystalline aggregates of the (123) phase. The introduction of Ag is claimed leading to the formation of multiphase ceramics. Ag is mainly distributed between the grain boundaries but a small amount enters into the (123) bulk lattice. Y & Nd do not alter the microstructure, but BaO & CuO appear as microphases [11].

2.2 Thin Films

Preparation and technological applications of thin HTS and CMR films are a research goal of the Superconductivity Group at Institute of Electronics, Bulgarian Academy of Science (IE BAS) under Professor A. Spasov [12-18]. Here are examples:

HTS. Good reproducible quality films are manufactured by magnetron sputtering, e.g. YBCO films on both sides of a $SrTiO_3$ substrate. The authors are interested in the microwave and optical transmission quality of the films for technological applications. A dependence of the surface resistance of thin YBCO films on the microwave (MW) current amplitude in microstrip resonators is observed at 77 K and interpreted in terms of hysteresis losses due to oscillations of the magnetic penetration depth at MW frequency. The magnetic response of double-sided films to normal quasistatic fields was modelled and compared with experiments at 77 K. The magnetic field effect on the parameters of microstrip resonators with a ferrite thin film component was studied. The results are applicable to optimizing magnetically tunable resonator devices with HTS and ferrire components [12]. The T_c distribution in YBCO films was probed: By step-wise removal of surface layers, a nonuniform in-depth T_c distribution was found. Films becoming more granular in-depth, the T_c distribution reflected conditions at the grain boundaries [15]. Spectroscopic measurements were carried out during optimization of a high-pressure dc-diode YBCO thin-film sputter deposition aimed at stabilizing the discharge and lowering the deposition temperature.[12] Weak links were investigated comprehensively [19].

CMR. Thin $La_{1-x}Ca_xMnO_3$ films were deposited by magnetron sputtering and their magneto-resistance measured [20,21]. The films grew epitaxial and oriented on a closely matched $SrTiO_3$ substrate. They exhibited 60% CMR at 50 kOe at $T_N = 270$ K [13]. The manufacture of a micro-electronic element with resistive response to low magnetic fields was implemented. The element is based on a modification of $La_{1-x}Sr_xMnO_3$ CMR exhibiting thin films in high fields. It applies as a magnetosensitive memory cell to information storage microelectronic devices [12].

2.3 Magnetic Tapes

Technological applications of HTS tapes and wires depend on the production of long-sized high-quality samples. Electric field *vs.* current density characteristics of mono- and multi-filamentary Bi-(2223)/Ag tapes were measured in 35–77 K range in background dc $\perp$ magnetic fields of up to 10 T at ac frequency of 37 Hz [22]. AC losses at 77 K were hysteretic and followed the $P \sim J^3$ law in fields up to 80 mT [23].

2.4 Single Crystals

Single crystals of ruthenides Gd_3RuO_7 and manganites $La_{1-x}Ca_xMnO_3$ are grown in the Crystal Growth Laboratory ISSP BAS under Dr. M. Gospodinov [24-29].

3 Raman spectra

HTS. An essential insight into high-T_c physics has been made at Micro-Raman facilities of Physics Faculty Sofia University (PF SU) under Professor Milko Iliev [30-32]. The microraman spectrometer provides for measurements on small microcrystals selected from a polycrystalline sample by a laser beam. The mode symmetry reflects the local site geometry but the smaller the illuminated spot the closer the symmetry to the genuine geometry, as it averages over fewer lattice spacings in a microsample than in a macrospectral experiment.

Raman studies were undertaken to follow the oxygen distribution in YBCO family. The oxygen-defficient $YBa_2Cu_3O_{7-\delta}$ system is insulating for $1 > \delta > 0.5$, its averaged phase being tetragonal, goes to type II orthorhombic phase near $\delta \sim 0.5$ and to type I orthorhombic phase at $\delta < 0.5$. These phases being distinguished by the oxygen distribution along the CuO_3 chains with $T_c = 0$, 60, and 90 K, respectively. Oxygen evolves easiest along the chains, then from the pyramidal vertexes and finally from the planes. The O isotope effect is faint before ^{18}O settles down in the planes [32]. Another addressed problem is the incorporation of Fe^{2+} substituting for Cu in $YBa_2(Cu_{1-x} Fe_x)_3O_{7-\delta}$ and $YBa(Cu_{1-x}Fe_x)_4O_8$. The Fe → Cu substitution depresses T_c dramatically. Careful Raman analysis indicated that substituting Fe atoms settle down at Cu sites along the chains altering the hole injection to the planes. Phonon modes in the $YBa_2Fe_3O_8$ and $YBaCuFeO_5$ by-phases were also identified [31].

Comprehensive microraman studies were made on superconducting materials of the Bi-Ca-Sr-Cu-O and Tl-Ba-Ca-Cu-O families by Professor V. Hadjiev in cooperation with M. Cardona's group in Germany. Of partucular interest were investigations of hydrogenated RBCO (R = Y, Gd) microsamples. Hydrogen incorporated at interstitial sites near Cu(I) and Cu(II) and reduced the hole concentration by substituting protons for holes. H absorption was also studied in at least two subsequent works [30,33]. The hydrogenization of nonsuperconducting samples indicated that they decomposed rather than absorbed H whose incorporation was thus dependent on the charge carriers [30]. Unique conclusions on a flow of electric currents in YBCO BaO plane were drawn from the observed configurational anisotropy of the apex-oxygen A_{1g} mode near 500 cm^{-1}. They were reaffirmed by observations of Ba B_{1g}-mode quenching, possibly by charge carriers in BaO plane. Heuristic conclusions were drawn on the YBCO A_{1g} apex-oxygen lineshape decomposed into several Gaussians, each relating to a definite structure.

CMR. Raman spectra of $La_{1-x}Ca_xMnO_3$ thin films were lately investigated aimed at the mechanism. Spectral changes across T_N indicated a metallic- to insulating-phase conversion along with strong reduction of JT distortions and changes in the interion magnetic exchange [34,35].

4 Mossbauer Spectra

The Superconductivity Group at PF SU investigated Mossbauer spectra of ^{57}Fe substituting for Cu(I) in the YBCO superconductor. The method is powerful as a probe for the local environment of incorporated Fe ions [33]. The temperature dependences of the resonant signal and electric resistivity correlated. A quadruple moment reduces dramatically in superconducting state: The signal coming from resonating valence bonds (RVB) localized at Fe(I) ions in normal state drops as RVB delocalize to form a superfluid condensate.

5 Thermal Properties

An equipment was designed and constructed at ISSP BAS for simultaneously following two thermal charactersitics of high-T_c materials [36]. The YBCO heat conduction coefficient and conduction of heat across a YBCO-Ruby boundary were measured.

A temperature hysteresis was established in 40–240 K for both thermal quantities, as was a thermal isotropy below 40 K. The hysteresis is taken as evidence for the role of apex oxygens in heat transfer, for the axial oxygen is bistable in YBCO lattice.

6 Theory

The basic theoretical HTS effort has focused on: (i) strongly correlated systems and (ii) vibronic or Jahn-Teller effects. (i) makes use of 't-J model', while (ii) assumes that Jahn-Teller configurational distortions lead to unconventional pairing.

6.1 Strongly Correlated Systems

Work on (i) was done in PF SU by Dr. T. Ivanov [37]. He used the mean field (MF) approach to Hubbard's Hamiltonian in the representation of the hole operators by auxiliary particles, holons and spinons. The method separates the charge carried by holons from the spin carried by spinons. There are two approaches called 'slave boson' and 'slave fermion', respectively, where the anticommutation relations are met on two formal statistics: bosonic holons and fermionic spinons (slave boson SB) and fermionic holons and bosonic spinons (slave fermion SF). In SB, superconductivity occurs as Bose condensation of holons, while in SF it appears by the formation of holon pairs mediated by spinon exchange.

In a pioneering SF work, Ivanov dealt with the holon-spinon interaction residual for MF. He derived a four-holon interaction term with a pairing potential which suggests holon Cooper pair formation. The main credit is to be given to Ivanov's result on the phase separation of holons and spinons into regions of seggregated charge and spin, which is observed experimentally. Another work by Ivanov is on the Kondo interaction between local and itinerant spins.

6.2 Vibronic Models

The vibronic work was initiated at ISSP BAS by a sporadic attempt to address the high-T_c problem by unconventional means. It was the late Professor Borissov's suggestion that pairing may involve a weak dispersive attraction between polarons. The nature of the dipolar moments being obscure, a way out was sought in the polarisation of vibronic polarons. The latter form under a Pseudo-JT mixing of electron states by lattice vibrations and carry a dipole moment, due to the breaking of inversion symmetry at a Cu site in high-T_c materials. The average dipole moment being vanishing because of flip-flops or rotation, two vibronic polarons may couple by virtue of fluctuating dipole moments like the dispersive Van-der-Waals interatomic coupling. Due to polaron band-narrowing, the vibronic polarizability exceeds largely the electrostatic polarizability. An effective VdW attraction occurs which overweighs the Coulomb repulsion and leads to bipolaron formation.

The problem of these vibronic polarons is that they are less mobile due to heavy itinerant mass resulting in low T_c. At the turn of the last decade, pairing mediated by apex oxygens of CuO_6 octahedra was a hit due to suggestions by K.-A. Muller. The idea behind dating back to the late J. Callaway is that the total energy of a two-hole unit lowers if each hole couples to a polarizable partner. Pairing may occur in the same plane or in parallel CuO_2 planes. Oxygen was pointed at as partner due to its larger polarizability and the apex site chosen for symmetry. Our pairing model utilized the vibronic-enhanced polarizability at the apex oxygen site..The vibronic partner pairing model is based on a two-level system in the adiabatic approximation similar to ones used for explaining the acoustic properties of glasses. In reference to HTS, the two-levels are applicable to ultrasonic attenuation, dielectric losses, and optical spectra [38].

P.W. Anderson is cited to say that the normal-state properties of high-T_c cuprates are the key to understanding the pairing mechanism. Recently, a joint Japanese-American group made considerable experimental contribution to understanding the normal state by extending it to lower temperatures $T \ll T_c$ by measuring the electric resistivity ρ in pulsed magnetic fields inhibiting pair formation. With no traces of magnetoresistivity, $\rho(T)$ dependences in single-layered $La_{2-x}Sr_xCuO_4$ were taken from 5 to 300 K for electric currents in-plane and along the c-axis. To explain the resistivities, we applied a model in which transient polarons form as hole carriers traverse Cu-O bonds. The hole transfer being coupled to a phonon mode, it goes across a double-well potential between two sites rich in in-plane Cu and apex-O states, respectively [39].

Itinerant broken-symmetry vibronic polarons have not been studied genuinely so far. We initiated a variational procedure based on Merrifield's method. Results for the extreme nonadiabatic energy range exhibited the small-polaron size. Itinerant JT polarons are worth studying in view of their relationship to CMR [40].

7 Conclusion

We are pleased to acknowledge that home scientists did play a role in the global research on two important fields of materials science, HTS and CMR. Further developments will show whether the home record is competitive to the rapidly growing demand for new technological advances.

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