Scientific session of the Division of General Physics and Astronomy of the Russian Academy of Sciences (27 October 1999)

A scientific session of the Division of General Physics and Astronomy of the Russian Academy of Sciences (RAS) was held at the P L Kapitza Institute for Physical Problems, RAS on 27 October 1999.

Two papers were presented at this session:

(1) Gavrichkov V A, Kuz'min E V, Ovchinnikov S G (L V Kirenskiĭ Institute of Physics of the RAS Siberian Branch and Krasnoyarsk State University, Krasnoyarsk) "Electronic structure and order parameter symmetry in high-temperature superconductors";

(2) **Golovashkin A I, Rusakov A P** (P N Lebedev Physics Institute, RAS and Moscow Institute of Steel and Alloys, Moscow) "Experimental studies of the thermal and electronic properties of $Ba_{1-x}K_xBiO_3$ and other perovskite-like oxide HTSC systems".

An abridged version of the papers is given below.

PACS numbers: **71.27** + **a**, 74.25Jb DOI: 10.1070/PU2000v043n02ABEH000707

Electronic structure and order parameter symmetry in high-temperature superconductors

V A Gavrichkov, E V Kuz'min, S G Ovchinnikov

1. Introduction

The electronic structure of layered copper-oxide hightemperature superconductors not only provides a clue to their superconducting properties but also gives an insight into their anomalies above T_c , in which latter respect significant progress has been made in recent years (see Refs [1-5] for reviews). Information on the band structure of a material is obtained most directly by angle-resolved photoelectron spectroscopy (ARPES) [3], which shows that for optimally and heavily doped superconducting materials the actual shape of a Fermi surface is close to that calculated in band theory using the density functional method, whereas the experimental band widths are several times less than the theoretical predictions. In the low doping regime, lowering the hole concentration first modifies the Fermi surface topology and gives rise to a pseudogap above T_c , and then leads to a metal-insulator transition and to the formation of an antiferromagnetic insulator. An adequate description of these phenomena requires that strong electron correlations be taken into account.

Uspekhi Fizicheskikh Nauk **170** 189–195 (2000) Translated by E G Strel'chenko; edited by A Radzig The present paper is divided into two parts. The first part presents calculated results on the electronic structure of copper oxides obtained by the generalized strong coupling (GSC) method taking the strong correlation explicitly into account within the framework of the multiband p-d model. The second part is devoted to analyzing the symmetry of the superconducting gap in a strongly correlated electron system.

2. The band structure of copper oxides following from the generalized strong coupling method

Since the Hubbard model and its three-band p-d generalization to CuO₂ layers account both for strong electron correlations in the system of copper $d_{x^2-v^2}$ holes and for hole hopping over oxygen atoms, and since at the same time there is a good deal of spectral evidence from XAS [6] and EELS [7] for a significant contribution from the d_{z^2} copper states, we have been trying for a long time to develop a multiband p-d model capable of incorporating the $d_{x^2-v^2}$ and d_{z^2} orbitals of copper and the p orbitals of oxygen in CuO₂ planes [8]. This model has recently been extended to include apical oxygen atoms [9]. For copper oxides there are two competing energies in the system: the strong intraatomic interactions of d electrons and the strong copper-oxygen hybridization, of which the former is readily accounted for in the local atomic approach, whereas the latter is taken into account trivially on going over to k space in the one-electron approach. We have proposed the GSC method to consider these opposite trends simultaneously [8]. In this, the lattice is divided into clusters for which the model Hamiltonian is exactly diagonalized and exact many-electron molecular orbitals $E_i(n)$ are constructed; the interaction between the clusters is then introduced as a perturbation. Unlike the conventional strong coupling method, where bands result from the dispersion of one-electron molecular orbitals (MO), in the GSC method the Fermi quasi-particle bands are due to the dispersion of one-electron resonances $\Omega_{ii} = E_i(n+1) - E_i(n)$, where *n* is the number of electrons in the cluster, and *i*, *j* is the set of remaining quantum numbers (spin, orbital moment, etc.). In the original approach of Ref. [8], the CuO₂ lattice was divided into two sublattices of linear CuO₂ clusters. The main advantage of such a division is that each atom belongs to one cluster only, making orthogonal the MOs of neighboring cells. In later work [10-12], a similar method was used to calculate a simpler three-band p-d model with the CuO₂ plane divided into CuO₄ clusters. Whereas this approach is preferable physically in that the cluster coincides with the unit cell and has the correct symmetry, the nonorthogonality of neighboring MOs (each oxygen atom belonging to two unit cells simultaneously) makes it more complex technically. This difficulty, however, has been overcome by explicitly constructing the Wannier functions [13]. Applying a similar procedure developed for a multiband p-d model with due regard for $d_{x^2-y^2}$ and d_{z^2}

copper orbitals [14, 15], we were able to perform GSC band structure calculations using symmetrical CuO_4 unit cells.

Conferences and symposia

We write the multiband p-d-model Hamiltonian in the generalized Hubbard form

$$H = \sum_{i\sigma} \varepsilon_{i} n_{i\sigma} + \sum_{\langle ij \rangle} \sum_{\sigma} t_{ij} (c^{+}_{i\sigma} c_{j\sigma} + \text{H.c.})$$

+
$$\sum_{i} U_{i} n_{i\uparrow} n_{i\downarrow} + \sum_{\langle ij \rangle} \sum_{\sigma\sigma'} V_{ij} n_{i\sigma} n_{j\sigma'}, \qquad (1)$$

where $c_i = d_{x^2-y^2}$, $d_{z^2}(p_x, p_y, p_z)$ if subscript *i* indicates the copper (oxygen) lattice site; ε_i is the energy of the corresponding atomic orbitals, calculated with account for the crystal field; $U_i = U_d$ or U_p , respectively; t_{ij} and V_{ij} are the two-center matrix elements for hopping and for the copper-oxygen (t_{pd} , V_{pd}) and oxygen-oxygen (t_{pp} , V_{pp}) Coulomb interaction, and finally $n_{i\sigma} = c_{i\sigma}^+ c_{i\sigma}$.

The exact diagonalization of the Hamiltonian (1) for a CuO₄ cluster is carried out separately in various sectors of the Hilbert space, identified by the number of holes $n_{\rm h}$ in the unit cell. In the vacuum sector, $n_{\rm h} = 0$, we have one state $|0\rangle = |d^{10}p^6\rangle$. In the $n_h = 1$ sector, one obtains usual onehole MOs of symmetry a_{1g} and b_{1g} , the b_{1g} MO resulting from the hybridization of the $d_{x^2-y^2}$ states with the oxygen p orbitals, and the a_{1g} MO coming about from mixing the d_{z^2} states of copper with the oxygen p states. The apical p_z orbitals mix in with the a_{1g} MOs as shown in Ref. [9]. In the two-hole $(n_{\rm h} = 2)$ sector we have a set of spin singlets and triplets of various orbital symmetry, the ground term and the closest excited term having the symmetries ${}^{1}A_{1g}$ and ${}^{3}B_{1g}$, respectively. While the Zhang-Rice singlet contributes significantly to the ¹A_{1g} MO [13], it is not the only contribution to this orbital. Whereas in the simplified threeband p-d model the Zhang-Rice triplet is higher in energy than the singlet, in a realistic multiband model the ${}^{3}B_{1g}$ triplet is close enough to the singlet, so much so that even a crossover between them becomes possible [16-18]. This proximity considerably affects the law of dispersion near the top of the valence band. The band structure of the undoped La₂CuO₄ in the antiferromagnetic phase in shown in Fig. 1, where the



Figure 1. Band structure of an undoped antiferromagnetic CuO₂ layer as in La_2CuO_4 or $Sr_2CuO_2Cl_2$.

empty conduction band is due to the dispersion of the a1g and b_{1g} MOs [i.e. of the resonances between the vacuum ($n_{\rm h} = 0$) and one-particle $(n_h = 1)$ terms], whereas the filled valence band is formed through the dispersion of the resonances between the one-hole and two-hole MOs. The valence band has a very complicated structure because of a large number of excited two-hole MOs. Notice here that the bands obtained by the GSC method are quasi-particle bands. Because of the strong electron correlations, these bands are rather unusual in that the number of states in each band depends on the electron density (the total number of states being conserved, of course) as well as external fields and temperature (due to the so-called filling factors $F_{ii} = n_i + n_i$, where n_i , n_i are the filling numbers of the corresponding initial and final states for the Ω_{ij} resonance [19]). Note that the law of dispersion near the top of the valence band is in good agreement with ARPES data for the other undoped oxide Sr₂CuO₂Cl₂ [20] which, like La₂CuO₄, is also an antiferromagnetic insulator (Fig. 2).



Figure 2. The law of dispersion near the top of the valence band of an undoped antiferromagnetic CuO_2 layer in comparison with the ARPES data of Ref. [20].

The hole doping of the material $(n_h = 1 + x)$ causes the redistribution of the filling numbers as calculated from the chemical potential self-consistency equation, with a consequence that the two-hole ground term is filled with probability x and that novel resonances within the insulating gap acquire nonzero spectral weight $\sim x$ [21]. The dispersion of these resonances produces an impurity band which overlaps with the valence band top (Fig. 3). The effect of doping is strongest close to the XM direction, i.e. the line $(\pi, 0) - (\pi, \pi)$, where according to ARPES data a gap opens on the Fermi surface in the $Bi_2Sr_2Ca_{1-x}Dy_xCu_2O_{8+x}$ system [22]. Also calculated by the GSC method were the concentration dependences of the X-ray absorption spectra (XAS) and photoelectron emission spectra (XPS), both of which revealed high-energy satellites (the peak C in Fig. 4) [23]. Although GSC calculations are fundamentally disadvantageous in that an appropriate Hamiltonian involves a large number of parameters which must be calculated separately or determined experimentally, in conceptual terms this approach has enabled a synthesis of Landau's and Hubbard's ideas - allowing one to introduce Fermi quasiparticles as a local generalization of the Fermi-liquid quasi-



Figure 3. Band structure of CuO₂ with hole concentration $n_h = 1 + x$ corresponding to La_{2-x}Sr_xCuO₄ for x = 0.10 (solid line) and x = 0.15 (dotted line).



Figure 4. X-ray absorption spectrum of the Cu K-radiation in La₂CuO₄: *I*, experiment; *2*, strong-correlation theory; *3*, one-electron theory [23]. Peak *C*, while observed experimentally, is absent in the one-electron theory.

particles and to calculate their dispersion by taking strong electron correlations explicitly into account.

3. Symmetry of the superconducting order parameter in strongly correlated electron systems

The symmetry of the superconducting state and the microscopic mechanism of high-temperature superconductivity are both the long-standing problems in the field. Today, there is strong evidence to suggest that the gap in hole superconductors has a d symmetry (see Refs [24, 25] for review), which can be explained in a natural way in terms of the spin-fluctuation pairing mechanism. At the same time, pairing in the electron superconductors $Nd_{2-x}Ce_xCuO_4$ appears to be of an s symmetry [26, 27]. Finally, Sr_2RuO_4 , the only copper-free superconducting oxide with the same layered structure, has the triplet gap of a p symmetry [28].

The triplet p-symmetry pairing in band theory is due to the ferromagnetic-type spin fluctuation exchange [29]. We have carried out the symmetry analysis of the superconducting gap using a simple model which, by analogy with the t-J model, is called the t-J-I model [30] and which includes strong electron correlations as well as nearestneighbor exchange interactions of antiferromagnetic (J) and ferromagnetic (I) types. The antiferromagnetic exchange interaction, as typical for oxides, is due to an indirect exchange via oxygen, whereas the ferromagnetic exchange interaction can result from the direct cationcation orbital overlap.

While cuprates are characterized by the σ -type bonding $d_{x^2-y^2}-p$ near the Fermi level, with $J \ge I$, in ruthenates we have π -type bonding $d_{xy}-p$, which permits a significant direct overlap of the d_{xy} orbitals of the neighboring Ru²⁺ ions, with $I \ge J$. The mean field theory for strongly correlated electrons involves, along with the usual BCS self-consistent equations for the gap and the chemical potential, the so-called 'constrain' condition which forbids the existence of local two-particle states. Within the t-J-I model this condition takes the form

$$\frac{1}{N} \sum_{k} \left\langle X_{-k}^{0\downarrow} X_{k}^{0\uparrow} \right\rangle = 0.$$
⁽²⁾

While s-type pairing does not fulfil this condition [31], p- and d-type gaps satisfy it automatically. In the t-J-I model, the possible solutions for the gap take the form

$$\Delta_{kl} = \lambda_l \psi_l(k) \Delta_l$$

where l = 1 and l = 2 for a p- and d-pairing, $\lambda_p = I/t$, $\lambda_d = (2J-I)/t$, and

$$\psi_{\rm p}(k) = \frac{1}{2} (\sin k_x + \sin k_y), \quad \psi_{\rm d}(k) = \frac{1}{2} (\cos k_x - \cos k_y).$$



Figure 5. Comparison of the concentration dependences of T_c in the p- and d-pairing channels; $\lambda_p = I/t$, $\lambda_d = (2J-I)/t$.

Gap equations for the p- and d-channels of pairing have the identical form

$$\frac{1}{\lambda_l} = \frac{1}{N} \sum_p \frac{|\psi_l(p)|^2}{2E_{pl}} \tanh \frac{E_{pl}}{2T}, \qquad (3)$$

where E_{pl} is the usual BCS-type gap excitation spectrum, but despite this similarity the solutions of Eqn (3) for the p- and t-type pairing behave differently.

The reason for this stems from the angular dependences of $|\psi_l(p)|^2$. Was the gap isotropic, the main contribution to the integral over the Brillouin zone would be determined by the narrow energy region near the van Hove singularity. For a d-type gap, the angular dependence acts to maintain the large van Hove-singularity contribution, whereas in the p-channel case the angular dependence is such as to cancel the singularity. For this reason, the numerical solution of Eqn (3) yields $T_c(p) \ll T_c(d)$ even for $\lambda_p = \lambda_d$ (Fig. 5). Thus, for optimally doped cuprates and ruthenates, where typically $\lambda_p = \lambda_d = 0.5$ and t = 0.1 eV, one finds $T_c(p) \approx 2.5$ K and $T_c(d) \approx 70$ K.

This work has been supported by the Krasnoyarsk regional Science Foundation through Grant No. 8F0032.

References

- Ginzburg V L, Maksimov E G Sverkhprovodimost 5 1543 (1992) [SPCT 5 1505 (1992)]
- 2. Dagotto E Rev. Mod. Phys. 66 763 (1994)
- 3. Shen Z X, Dessaw D S Phys. Rep. 253 1 (1995)
- Loktev V M Fiz. Nizk. Temp. 22 3 (1996) [Low Temp. Phys. 22 1 (1996)]
- Ovchinnikov S G Usp. Fiz. Nauk 167 1043 (1997) [Phys. Usp. 40 993 (1997)]
- 6. Bianconi A et al. Physica C 162-164 209 (1990)
- 7. Romberg H et al. *Phys. Rev. B* **41** 2609 (1990)
- 8. Ovchinnikov S G, Sandalov I S Physica C 161 607 (1989)
- Gavrichkov V A, Ovchinnikov S G Fiz. Tverd. Tela (St. Petersburg) 40 184 (1998) [Phys. Solid State 40 163 (1998)]
- 10. Jefferson J H *Physica B* **165–166** 1013 (1990)
- 11. Lovtsov S V, Yushankhai V Yu Physica C 179 159 (1991)
- 12. Jefferson J H, Eshes H, Feiner L F Phys. Rev. B 45 7959 (1992)
- 13. Zhang F C, Rice T M Phys. Rev. B 37 3759 (1988)
- 14. Feiner L F, Jefferson J H, Raimondi R Phys. Rev. B 53 8751 (1996)
- 15. Feiner L F, Jefferson J H, Raimondi R Phys. Rev. B 53 8774 (1996)
- 16. Kamimura H, Eto M J Jpn. J. Phys. Soc. 59 3053 (1990)
- 17. Eshes H, Tjeng L H, Sawatzky G A Phys. Rev. B 41 288 (1990)
- Ovchinnikov S G Pis'ma Zh. Eksp. Teor. Fiz. 64 23 (1996) [JETP Lett. 64 25 (1996)]
- Zaĭtsev R O Zh. Eksp. Teor. Fiz. 70 1100 (1976) [Sov. Phys. JETP 44 652 (1976)]
- 20. Wells B O et al. Phys. Rev. Lett. 74 964 (1995)
- Ovchinnikov S G Zh. Eksp. Teor. Fiz. 102 534 (1992) [Sov. Phys. JETP 75 283 (1992)]
- 22. Marshall D S et al. Phys. Rev. Lett. 76 4841 (1996)
- 23. Avramov P V, Ovchinnikov S G Zh. Strukt. Khim. 40 131 (1999)
- 24. Scalapino D J Phys. Rep. 250 329 (1995)
- Izyumov Yu A Usp. Fiz. Nauk 169 225 (1999) [Phys. Usp. 42 215 (1999)]
- 26. Wu D H et al. *Phys. Rev. Lett.* **70** 85 (1993)
- 27. Stadlober B et al. Phys. Rev. Lett. 74 4911 (1995)
- 28. Rice T M, Sirist M J. Phys.: Condens. Matter 7 643 (1995)
- 29. Akhiezer A I, Pomeranchuk I Ya *Zh. Eksp. Teor. Fiz.* **36** 859 (1959) [*Sov. Phys. JETP* **9** 605 (1959)]
- Kuz'min E V, Ovchinnikov S G, Baklanov I O Zh. Eksp. Teor. Fiz. 116 655 (1999) [JETP 89 349 (1999)]
- Plakida N M, Yushankhai V Yu, Stasyuk I V Physica C 160 80 (1989)

Experimental studies of the thermal and electronic properties of $Ba_{1-x}K_xBiO_3$ and other perovskite-like oxide HTSC systems

A I Golovashkin, A P Rusakov

The basic properties of the cuprate high-temperature superconductors (HTSC) are attributed to the antiferromagnetic (AF) ordering of Cu ions known as the spin density wave (SDW). Recently, however, a number of anomalies have been discovered which cannot be explained by this ordering mechanism alone. To provide an insight into their origin, the noncuprate HTSC systems $Ba_{1-x}K_xBiO_3$ (BKBO) and $BaPb_xBi_{1-x}O_3$ (BPBO) showing similar anomalies have been studied in this work.

Neutron diffraction studies have shown that doping causes a strong softening of the high-frequency portion of the BKBO phonon spectra [1]. The analysis of the dispersion curves $\omega(\mathbf{O})$ has further shown that in the metallic phase of an HTSC the high-frequency longitudinal optical phonons $\omega_{\rm LO}(\mathbf{Q})$ are soften anomalously strongly on doping [2-4]. For wave vectors **Q** near the boundary of the Brillouin zone, the frequencies $\omega_{LO}(\mathbf{Q})$ become lower than the transverse optical frequencies $\omega_{TO}(\mathbf{Q})$ (' ω_{LO} anomaly'). For all the HTSCs investigated — BKBO, $La_{2-x}Sr_xCuO_4$ (LSCO), and YBa₂Cu₃O_{7-x} (YBCO) — the anomalous dispersion of ω_{LO} was observed only along [100] and never along other directions, in particular [110]. Notice here that if AF ordering was the dominant ordering mechanism along [110], there would necessarily be ω_{LO} anomalies in the same direction, which is not the case experimentally.

We have shown that for the BKBO, BPBO [5, 6], and LSCO [7] systems at low temperatures *T* the linear expansion coefficient $\alpha(T)$ is anomalous (negative). This effect is observed only in high-quality samples. Similar anomalies have also been seen in YBCO [8] and Bi-2219 [9]. In single-crystal samples of LSCO, YBCO, and Bi-2212, $\alpha(T)$ is anisotropic — the less so, the higher the doping level.

An interesting point about the HTSC systems is the anomalously strong magnetic-field dependence of the thermal expansion, $\alpha(H)$. Up to 4 T, the region of negative values of α is observed to shrink, while at the same time moving towards lower temperatures in both cuprate and copper-free HTSCs [10].

Optical measurements reveal that while the energy gap between the valence band and the conduction band in the BKBO and BPBO systems narrows with doping, it still remains observable even in the metallic phase, provided the material is moderately doped [11-14]. Evidence for this has also been seen in LSCO using the ultrahigh-resolution (7 MeV) photoelectron emission method [15, 16] and in Bi-2212 using an X-ray absorption technique [17]. Thus, the 'metallic' phase is that of a degenerate semiconductor both for copper-free and cuprate HTSCs.

Another common anomaly of HTSC systems is the existence of EPR signals in the 'half field' with a g factor of about 4. This 'forbidden' signal is observed in the presence of localized triplet pairs. The absorption line with $g \approx 4.2$ (in addition to that with $g \approx 2.1$) was observed in EPR absorption measurements on high-quality BKBO and BPBO

PACS numbers: 74.25.-q, 74.72-h

DOI: 10.1070/PU2000v043n02ABEH000708