

Oxygen-hole pairs drive bond order and superconductivity in bismuth oxides

1. Unveiling the superconducting mechanism of $\text{Ba}_{0.51}\text{K}_{0.49}\text{BiO}_3$

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2. Oxygen holes and hybridization in the bismuthates

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Superconductivity in hole-doped BaBiO_3 (BBO), namely, $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (BKBO) with T_c as high as ~ 30 K, was discovered immediately after the discovery of high- T_c cuprates [1]. (Prior to them, Pb-doped $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ BPBO with a lower T_c of ~ 12 K had been known for more than ten years [2].) BKBO differs from the cuprates in that they have three-dimensional (3D) crystal and electronic structures against the two-dimensional (2D) electronic structures of the cuprates. Moreover, BKBO does not contain transition elements and hence no magnetism should play a role in Cooper-pairing mechanism nor in competing order. Indeed, “charge-density-wave (CDW)” states have been known as phases competing with superconductivity in BKBO. In the “CDW” states, the BiO_6 octahedra are expanded and contracted alternatingly. The “CDW” formation is closely related to the instability of the Bi^{4+} ($6s^1$) valence state toward the charge-disproportionated Bi^{3+} ($6s^2$) + Bi^{5+} ($6s^0$), referred to as valence skipping [3]. This would naturally lead to bipolaron formation of doped holes and to a Bose-Einstein condensation (BEC) of bipolarons [4]. Even if two holes are not localized on one Bi atom but are extended over many Bi atoms, the on-site attractive interaction between two holes may survive and help the s -wave superconductivity. In fact, BKBO is found to be a strong-coupling BCS superconductor [5]. The above scenario appeared consistent with experiment, but some fundamental questions remain, too, and the problem turned out to be much more complicated and deeper than expected:

The first question is why electron-phonon coupling strength evaluated using the local-density approximation (LDA) calculation is too weak to explain the T_c of BKBO within BCS theory. Such a difficulty was, however, not unexpected because BKBO is basically an ionic crystal with low carrier density and hence long-range Coulomb interaction may not be fully screened as in typical metals and alloys, for which BCS theory was initially developed. In fact, it has been shown that long-

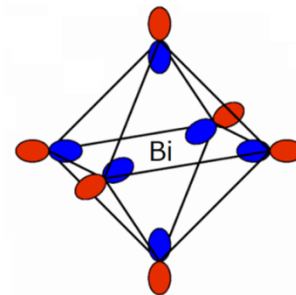


Fig. 1 A_{1g} -symmetry molecular orbital consisting of six oxygen p atomic orbitals surrounding the Bi atom in the BiO_6 octahedron [7].

range Coulomb interaction has to be treated beyond LDA (as in the GW approximation of the self-energy) in order to deduce electron-phonon coupling that is strong enough to explain the observed high T_c [6]. In the first recommended article (paper 1), Wen *et al.* performed ARPES measurements on BKBO and found that the width of the band which crosses the Fermi level (E_F) was larger than that predicted by LDA calculation for the first time. They have also shown that the increased band width is reproduced by calculation which treats the exchange potential for long-range Coulomb interaction beyond LDA, namely, in the Fock approximation. However, because band widening usually occurs simultaneously with band narrowing, which is caused by on-site Coulomb interaction and also produces incoherent spectral features away from E_F , it is generally not easy to disentangle the two effects unambiguously from experimental data [7].

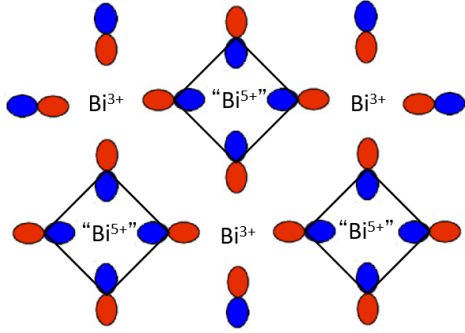


Fig. 2 Breathing distortion of the BiO_6 octahedra. Hole pairs reside in the A_{1g} molecular orbitals of the compressed “ Bi^{5+} ” O_6 octahedra depicted by black squares.

to a bond-ordered $\text{Bi}^{3+}(6s^2) + \text{“Bi}^{5+}\text{”}(6s^2\bar{L}^2)$ state. Here, \bar{L} denotes a hole in the A_{1g} molecular orbital of the compressed octahedron and \bar{L}^2 denotes a pair of holes on the same molecular orbital. The semiconducting gap opens in BBO by the breathing distortion and is further enhanced by the tilting of the BiO_6 octahedra [8,9]. In the second recommended article (paper 2), Khazraie *et al.* analyzed LDA results and found that the Bi 6s level is located below the oxygen p band, classifying BBO as a negative charge-transfer-energy (negative- Δ) insulator, originally proposed for the insulating Cu^{3+} oxide NaCuO_2 [10]. They also deduced a single-band model, a minimum band model to describe the low-energy properties of BBO and BKBO, and estimated the electron-phonon interaction to be strong enough to explain the observed T_c . Here, long-range Coulomb-exchange was not explicitly taken into account, but it may have been included implicitly through the orbital energies. As for the on-site Coulomb interaction, it may be negligible for Bi 6s electrons while it may not be negligible for oxygen p electrons [11], which dominate electronic states near E_F .

Because a hole pair resides in the compressed “ Bi^{5+} ” O_6 octahedron in BBO, attractive interaction between two A_{1g} holes on the same octahedron may survive after the long-range bond order has been disrupted by hole doping as long as the breathing distortion survives as a fluctuation. As the hole concentration decreases, the T_c increases. This is probably because the hole pairs would become long-lived and the transition would approach the BEC of bipolarons. Unfortunately, the bond-order instability sets in at $\sim 35\%$ hole doping and one cannot go to the BEC regime BKBO so far. Within the BCS scenario, the extremely strong Bi-O hybridization that is sensitive to the Bi-O bond length is expected to lead to a strong coupling of electrons at E_F with the breathing phonons around $\mathbf{q} = (\pi, \pi, \pi)$.

So far, emphasis has been made on the differences rather than similarities between BKBO and the cuprates, but it should be noted that the band structures of sufficiently hole-doped cuprates, where

The second question is how to consider the $\text{Bi}^{5+}(6s^0)$, $\text{Bi}^{4+}(6s^1)$, and $\text{Bi}^{3+}(6s^2)$ configurations in the presence of strong Bi 6s-oxygen p hybridization. In fact, LDA calculation has shown that states near E_F is dominated by oxygen p orbitals with some admixture of Bi 6s orbitals, meaning that doped holes in BKBO predominantly enter oxygen p orbitals rather than Bi 6s orbitals [8]. In momentum space, the strongest Bi-O hybridization occurs at the Brillouin-zone corner $\mathbf{k} = (\pi, \pi, \pi)$, where the bonding-antibonding splitting exceeds 10 eV! In real space, the same strong hybridization occurs between the Bi 6s orbital and a molecular orbital of the fully symmetric (A_{1g} -symmetry) linear combination of six oxygen p orbitals surrounding the Bi atom, as shown in Fig. 1. Breathing distortion, i.e., expansion and contraction of alternating BiO_6 octahedra, takes place as shown in Fig. 2: There is no such charge disproportionation as $\text{Bi}^{3+}(6s^2) + \text{Bi}^{5+}(6s^0)$ but there are alternating longer Bi^{3+} -O and shorter “ Bi^{5+} ”-O bonds leading

magnetism has disappeared, have common features with BKBO: The Cu $3d_{x^2-y^2}$ -O $2p$ hybridization is as strong as Bi $6s$ -O $2p$ and the bonding-antibonding splitting reaches ~ 9 eV at the 2D Brillouin-zone corner, $\mathbf{k} = (\pi, \pi)$ [12]. In real space, this corresponds to the strong hybridization between the Cu $3d_{x^2-y^2}$ orbital and the B_{1g} -symmetry molecular orbital consisting of four surrounding oxygen p orbitals of the CuO_4 plaquette, leading to the formation of the Zhang-Rice singlet from Cu^{2+} and a doped oxygen hole [13]. The breathing phonons around $\mathbf{q} = (\pi, \pi)$ are, therefore, coupled to electrons near E_F and induce oxygen hole pairs in analogy to Fig. 2. The attractive interaction between two holes in a CuO_4 plaquette, however, will not help the d -wave pairing since the pairing is stabilized by attractive interaction between neighboring plaquettes but destabilized by on-plaquette attractive interaction.

In conclusion, the new lessons from BKBO discussed in the recommended papers, namely, the importance of long-range Coulomb-exchange and the molecular-orbital character of oxygen holes should hold for the cuprates and have to be further explored. The question of the nature of intra- and inter-atomic correlations and their coupling to lattice distortion, which lead to the "valence skipping" in Bi and about 15 other elements when they form ionic insulators [3], is still to be adequately answered, but it may be possible to do so by using the techniques given in the recommended papers.

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