Superconducting-insulating quantum phase transition associated with valence change in compressed perovskite bismuth-oxides

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Abstract

Searching for a universal trend by the same tuning method in different high-temperature superconductors with a similar crystal structure is a common strategy to find clues for a better understanding the superconducting mechanism in a unified way. It is known that the hole-doped bismuth-oxide Ba$_{1-x}$K$_x$BiO$_3$ possesses a similar perovskite structure to that of the hole-doped copper-oxide (cuprate) superconductors but also holds a comparatively high superconducting transition temperature. In this study, we report the first observation of the pressure-induced quantum phase transition (QPT) from superconducting to insulating states in a series of Ba$_{1-x}$K$_x$BiO$_3$ single-crystal samples. A similar QPT has also been observed recently in the compressed cuprate superconductors. Significantly, we found that the QPT observed in Ba$_{1-x}$K$_x$BiO$_3$ is intriguingly associated with the valence change of the Bi ions in the material. These results lead us to propose that the pressure-induced valence change from Bi$^{3+}$ to Bi$^{5+}$ destroys the hole-doping effect on stabilizing the conductivity and corresponding superconductivity. By comparing the high-pressure behaviors observed in these two kinds of oxides, we identified another prominent feature shared by them - the more the hole-doping concentration, the higher the critical pressure required for driving the QPT.

Main Text

Soon after the discovery of high-temperature superconductors in perovskite copper-oxides (cuprates), another type of high-temperature perovskite superconductors was found in bismuth-oxide Ba$_{1-x}$K$_x$BiO$_3$, (bismuthates). Such a finding ignited a new excitement in the community. Although they possess the same perovskite structure, the superconductivity in these materials develops from different ordered states upon hole doping. The superconductivity in cuprates emerges in the proximity of an antiferromagnetic (AFM) ordered state, while the superconductivity in bismuthates appears near a charge-density-wave (CDW) ordered state. It suggests that the suppressed ordered state of the AFM or the CDW is closely associated with the emergence of superconductivity in these superconductors. In the past few decades, many experimental works on the perovskite cuprates and bismuthates have been reported. However, understanding their high-temperature superconductivity in a unified way still stands as a grand challenge due to the seemingly diversified underlying physics of electron correlations, which fundamentally determines the mechanism of the high-temperature superconductivity. Therefore, searching for the universal trends through the same tuning method to investigate the different types of high-$T_c$ superconducting oxides with a similar crystal structure is expected to be a crucial step toward a better understanding their universal mechanism of superconductivity.

Pressure is an effective method to tune superconductivity beyond chemical doping, because it can dramatically manipulate the crystal and corresponding electronic structures by compressing the lattice without adding the complexity of chemistry. As a result, it has been widely adopted as an independent control parameter in the studies on superconductivity. The pressure-induced variations of the superconducting transition temperature ($T_c$) have been observed in many of the layered-perovskite
cuprates\textsuperscript{26-33}. Intriguingly, a pressure-induced quantum phase transition from a superconducting state to an insulating-like state was found recently in cuprate superconductors\textsuperscript{1}, which presents universally in the samples - regardless of doping levels and numbers of the copper-oxide plane in a unit cell. These experimental results renewed the traditional knowledge that applying pressure usually enhances the bandwidth and makes the material more metallic\textsuperscript{34}. The central questions for this surprising phenomenon are: What is the intrinsic root of driving such a QPT from a superconducting to an insulating-like state, and what is the determining factor in stabilizing high-\(T_c\) superconductivity? In this study, we performed the combined measurements of high-pressure transport, x-ray diffraction and absorption for the perovskite bismuthate \(\text{Ba}_{1-x}\text{K}_x\text{BiO}_3\), hoping to reveal some possible common physics of these two hole-doped superconducting perovskite oxides.

The single crystals were grown by a modified electrochemical method [see Supplementary Information - SI]. The single crystal diffraction measurements on one of our superconducting samples, \(\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3\), indicate that it crystallizes in a cubic unit cell at room temperature with lattice parameters \(a = 4.340\ \text{Å}\) and space group Pm-3m (No.221), as shown in Fig.1a-1d. The diffraction spots for the \((0kl)\), \((h0l)\) and \((hk0)\) zones demonstrate that the sample is of high quality. Since \(\text{Ba}_{1-x}\text{K}_x\text{BiO}_3\) is sensitive to air and moisture, we loaded each of the samples into diamond anvil cell (DAC) in a glovebox, then took the DAC from the glovebox and performed high-pressure resistance measurements.

As shown in Fig.1e, the plot of resistance versus temperature measured at 1.2 GPa shows a sudden drop at \(\sim 31\ \text{K}\) and subsequently reaches a zero-resistance state. Applying a magnetic field, the drop shifts to the lower temperature, signaling a superconducting transition. The superconducting transition was confirmed by the measurements of the magnetic moment in zero-field cooling (ZFC) and field-cooling (FC) modes, which show diamagnetic throws at \(\sim 31\ \text{K}\) (Fig.1f). These results are in accordance with the results reported previously\textsuperscript{35-38}.

Next, we conducted the high-pressure resistance measurements on the superconducting \(\text{Ba}_{1-x}\text{K}_x\text{BiO}_3\) samples with different doping concentrations. Figure 2 shows the results of resistance versus temperature obtained at different pressures for the \(x=0.40\) sample with \(T_c = 31\ \text{K}\) (Fig.2a), the \(x=0.43\) sample with \(T_c = 28.5\ \text{K}\) (Fig. 2b), the \(x=0.52\) sample with \(T_c = 18.1\ \text{K}\) (Fig.2c) and the \(x=0.58\) sample with \(T_c = 14.1\ \text{K}\) (Fig.2d). It is found that these samples exhibit the same high-pressure behavior: \(T_c\) displays slight variation up to the first critical pressure \((P_{c1})\) and then exhibits a monotonous decrease with increasing pressure until the second critical pressure \((P_{c2})\) where the superconducting state is fully suppressed, and subsequently an insulating state appears. We repeated the measurements on new samples and found that the results were reproducible (see SI).

The pressure-\(T_c\) phase diagrams for the measured samples with different doping concentrations are summarized in Fig.3a, which is established based on \(T_c\) versus pressure for each of the samples (Fig.3b-3e). It is seen that more doping reinforces the decrease of the \(T_c\) value, until a universal quantum phase
transition from a superconducting (SC) state to an insulating (I) state. Intriguingly, it can be seen that the higher the doping concentration, the higher the critical pressure required for driving the QPT (Fig. 3f).

It is generally believed that the emergence of the QPT in materials is associated with the change in crystal and electronic structures. We performed high-pressure synchrotron X-ray diffraction measurements at 300 K for the $x=0.40$ sample at beamline 4W2 at the Beijing Synchrotron Radiation Facility to clarify the possible microscopic origin. No structural phase transition is found in the pressure range up to 37.4 GPa (see SI), confirming that the observed QPT in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ is not associated with any pressure-induced structural phase transition. Furthermore, we note that, although the declining rate of the lattice parameter $a$ varies slightly in the pressure range covering the entire superconducting regime, the response of $T_c$ to pressure displays a drastic change (Fig. 4a and 4b), i.e., $T_c$ exhibits slight variation below $P_{c1}$, while in the range between $P_{c1}$ and $P_{c2}$ displays a monotonous decrease, where the lattice constant dependence of pressure shows a slower decreasing tendency. Interestingly, the robust superconductivity below $P_{c1}$ in the compressed bismuthate superconductors is entirely different from what is seen in the copper oxide superconductors, whose $T_c$ is sensitive to the applied pressure\textsuperscript{1,39}. Such an unusual superconducting behavior observed in the compressed bismuthate superconductors has been only found in some elemental and alloy superconductors\textsuperscript{40-42}. This is the first time to discover the $T_c$ ‘plateau’ in pressurized high-temperature superconductors, the underlying physics of which calls for further investigations. In order to focus on the QPT, a key theme of this study, we will report our investigation on the exotic $T_c$ ‘plateau’ in a separated paper\textsuperscript{43}.

To understand the observed phenomenon, we plotted the pressure dependence of resistance ($R/R_{1.2 \text{ GPa}}$) that was measured just above the superconducting transition temperature in Fig. 4c. We found that $R/R_{1.2 \text{ GPa}}$ began to increase at the pressure above $P_{c1}$, where $T_c$ starts to decrease (Fig. 4a). Upon further compression, the resistance rises rapidly (see inset of Fig. 4c), in the meantime, $T_c$ declines dramatically. This suggests that the insulating phase starts at $P_{c1}$, and then gets more and more prevailed by elevated pressure between $P_{c1}$ and $P_{c2}$. When pressure is close to $P_{c2}$, superconducting puddles immerse in an insulating background, giving rise to a weak link superconductivity. Our measurements of the superconducting transition under different magnetic fields support the existence of such a weak link superconductivity - we found that the sample subjected to a pressure between $P_{c1}$ and $P_{c2}$ loses its zero-resistance state, and its onset $T_c$ can be destroyed by a relatively small magnetic field (see SI).

To investigate the origin of the QPT found in the bismuthate superconductors, we conducted high-pressure X-ray absorption measurements for the $x=0.40$ and 0.52 samples at beamlines of Dynamic and 15U at Shanghai Synchrotron Radiation Facility, respectively. Representative $L_{\text{III}}$-edge X-ray absorption spectra of the two samples collected at different pressures can be found in SI. The ambient-pressure result indicates that the two $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ samples bear a mixed valence state, in good agreement with the results reported\textsuperscript{44-46}. To show the pressure-induced $T_c$ change with the evolution of the mean valence (n) of Bi ions in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, we extracted pressure dependence of n for the $x=0.40$ sample (Fig. 4d). It is
found that \( n \) increases monotonously from 3.8 at ambient pressure to 5 at \( \sim P_{c2} \), where the superconducting-insulating transition takes place. Further increasing pressure up to 41.7 GPa, the value of \( n \) maintains at 5. Similar results are also observed from the \( x=0.52 \) sample (see SI). Considering the unsteady nature of the perovskite crystal structure of the \( \text{Ba}_{1-x}\text{K}_x\text{BiO}_3 \) superconductors, we propose that the transformation from a mixed valence state to a single-valence state of Bi ions is associated with the superconducting-insulating transition. Thus, a possible root for the transition could be suggested that applying pressure distorts the Bi-O bond and thus imposes the electron configuration of the Bi ions from Bi\(^{3+}\)(5\(d^0\)6\(s^2\)6\(p^0\)) to Bi\(^{5+}\)(5\(d^{10}\)6\(s^0\)6\(p^0\))\(^{47-49}\). It is noted that, when Bi\(^{3+}\) ions no longer exist in the sample, the system is compelled to enter an anomalous insulating state, instead of a metallic state as predicted by the band structure theory\(^8\). This implies that the electronic state of Bi\(^{3+}\) plays a vital role in stabilizing superconductivity.

The observed quantum criticality phenomenon in the compressed \( \text{Ba}_{1-x}\text{K}_x\text{BiO}_3 \) superconductors is similar to what is seen in the compressed cuprate superconductors\(^1\). To investigate the possibility of the pressure-induced valence change in bismuth-bearing cuprates, we performed high-pressure X-ray absorption measurements on the hole-doped superconducting \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+d} \) up to 48.2 GPa, where the sample moves in an insulating-like state\(^1\). The pressure dependence of main valence (\( n \)) of Bi ions shows that, unlike the high-pressure behavior observed from \( \text{Ba}_{1-x}\text{K}_x\text{BiO}_3 \), no dramatic valence change was found (see SI). The deep-inside physics of the pressure-induced insulating state in these two types of superconductors calls for further investigations.

The high-pressure phenomenon found in both hole-doped copper- and bismuth-oxide perovskite superconductors is highly unusual, renovating our knowledge about the high-\( T_c \) superconductors that they ought to turn a metallic state after the superconductivity is fully suppressed\(^34\). Our results indicate that the hole-doping effect on these superconducting materials is damaged by applying pressure. Moreover, an important commonality is also revealed from the high-pressure behavior of these two types of superconducting oxides - the heavier the hole doping, the higher the pressure required to peter out the hole-doping effect on stabilizing the superconductivity and finally realize the QCT. However, the QPT found in these two superconducting oxides may have different origins. One of the possible scenarios for the observed QPT is proposed here. For cuprates, the pressure may compel the electrons from sites of the apical oxygen to move to the oxygen sites in the superconducting CuO\(_2\) plane of cuprates\(^7\), as a result of occupying the hole sites in the plane. Such a pressure-induced ‘traffic re-jam’ of electrons may make the material to be insulated again\(^16\). While for the bismuthates, the pressure-induced valence change possibly counteracts the doping effect on stabilizing the superconductivity, finally expediting the system to enter the insulating state.

In order to check our proposed scenario, we performed pressure-releasing experiments on the compressed \( \text{Ba}_{0.57}\text{K}_{0.43}\text{BiO}_3 \) sample. We found that the compressed sample in the insulating state recovered to its superconducting state, initially at 13.7 GPa, and reached a zero-resistance state at 5.4 GPa [see SI]. More
significantly, we found that releasing the pressure makes the mean valence of Bi ions recovered from $5^+$ where the sample is in an insulating state to $3.8^+$ where the sample is in a superconducting state (Fig. 4d). The phenomenon of the reversible superconductivity is like what is found in the perovskite cuprate superconductors\textsuperscript{1}, indicating that the pressure-induced insulating state in both of the oxides is metastable. These results further support our explanation for the microscopic physics of the superconducting-insulating transition: the pressure-induced valence change from Bi$^{+3}$ to Bi$^{+5}$ is the fundamental root for realizing the superconducting-insulating transition in Ba$_{1-x}$K$_x$BiO$_3$. The consequence of decompression releases the pressure-induced metastable distortion of the Bi-O bond\textsuperscript{50} and thus allows the insulating state to return to the superconducting state.

The universal high-pressure behavior about the QPT and their peculiarities found in these two types of perovskite superconducting oxides highlight that the high-$T_c$ superconductivity of the perovskite superconductor are generally driven by the interplays among the unstable lattice, orbital, spin, and charge degrees of freedom in the superconducting ground state. As no detailed information in available literature could appropriately explain the observed high-pressure behaviors found in these hole-doped perovskite superconducting oxides in a unified way, it deserves further investigations with other advanced experimental probes and sophisticated theoretical studies.

**Declarations**

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Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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**Figures**

(a) - (c) The single crystal x-ray diffraction patterns for the (0kl), (h0l) and (hk0) zones of the sample, respectively, measured at 300 K. (d) Schematic crystal structure of the sample, describing the refined crystal structure with a cubic unit cell. (e) Resistance as a function of temperature at 1.2 GPa under different magnetic fields. (f) Magnetic moment versus temperature in both field-cooled (FC) and zero-field-cooled (ZFC) modes at ambient pressure.

**Figure 1**

*Structure characterization and transport measurements on the perovskite superconductor Ba$_{0.6}$K$_{0.4}$BiO$_3$. (a)-(c) The single crystal x-ray diffraction patterns for the (0kl), (h0l) and (hk0) zones of the sample, respectively, measured at 300 K. (d) Schematic crystal structure of the sample, describing the refined crystal structure with a cubic unit cell. (e) Resistance as a function of temperature at 1.2 GPa under different magnetic fields. (f) Magnetic moment versus temperature in both field-cooled (FC) and zero-field-cooled (ZFC) modes at ambient pressure.*
Figure 2

Temperature dependence of resistance for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ at different pressures. Plots of resistance versus temperature for the $x=0.40$ sample measured in the pressure range 1.2 - 44.6 GPa (a), for the $x=0.43$ sample measured in the pressure range 1.1 - 37.5 GPa (b), for the $x=0.52$ sample measured in the pressure range 1.3 - 38.3 GPa (c) and for the $x=0.58$ sample measured in the pressure range 1.4 - 37.0 GPa (d). All samples exhibit the same behavior - an insulating-like state appears above a critical pressure. The inset of each figure displays an enlarged view of the resistance in the lower-temperature regime.
Figure 3

Pressure - Temperature phase diagrams for the Ba$_{1-x}$K$_x$BiO$_3$ superconductors with different doping concentrations. (a) Pressure dependences of superconducting and insulating transition temperatures for the $x=0.40$, 0.43, 0.52 and 0.58 samples, showing that the $x=0.40$, 0.43, 0.52 samples undergo a universal quantum phase transition from a superconducting state to an insulating-like state. The temperatures of the superconducting and insulating transition were determined by the same method.
The acronym SC and I stand for the superconducting state and insulating state, respectively. For the $x=0.58$ sample, the superconducting-insulating transition seems to require a higher pressure. (b-e) The mapping information of temperature- and pressure-dependent resistance (see the color scale) for the samples, together with the phase diagrams established by the experimental results. (f) Plot of doping concentration ($x$) versus $P_{c2}$.

Figure 4
Pressure dependence of superconducting transition temperature ($T_c$), lattice parameter ($a$), $R/R_{1.2GPa}$ and mean valence ($n$) for the $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ sample. (a) Pressure-$T_c$ phase diagram, showing the three regions: $T_c$ presents little variation below $P_{c1}$ (left), monotonous decrease below $P_{c2}$ (middle), the insulating state appeared at pressure above $P_{c2}$ (right). (b) Plot of lattice parameter $a$ versus pressure. (c) Normalized resistance ($R/R_{1.2GPa}$) as a function of pressure. (d) Pressure dependence of mean valence ($n$) of Bi ions in $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$. The pink circles are the data measured upon increasing pressure, the green diamond is the data measured at releasing pressure about 3.7 GPa, demonstrating that the valence returns from $\text{Bi}^{5+}$ to $\text{Bi}^{+3.8}$ that is in good agreement with the superconductivity recovery observed. The orange and blue solids are the mean valence of the reference material $\text{Bi}_2\text{O}_3$ and $\text{NaBiO}_3$, which is employed to identify the peak position of $\text{Bi}^{+3}$ and $\text{Bi}^{5+}$ of the measured sample, respectively.

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