Large oxygen-isotope effect in Sr$_{0.4}$K$_{0.6}$BiO$_3$: Evidence for phonon-mediated superconductivity

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Abstract

Oxygen-isotope effect has been investigated in a recently discovered superconductor Sr$_{0.4}$K$_{0.6}$BiO$_3$. This compound has a distorted perovskite structure and becomes superconducting at about 12 K. Upon replacing $^{16}$O with $^{18}$O by 60-80%, the $T_c$ of the sample is shifted down by 0.32-0.50 K, corresponding to an isotope exponent of $\alpha_O = 0.40(5)$. This isotope exponent is very close to that for a similar bismuthate superconductor Ba$_{1-x}$K$_x$BiO$_3$ with $T_c = 30$ K. The very distinctive doping and $T_c$ dependencies of $\alpha_O$ observed in bismuthates and cuprates suggest that bismuthates should belong to conventional phonon-mediated superconductors while cuprates might be unconventional superconductors.
The discovery of high-temperature superconductivity near 30 K in the nonmagnetic cubic perovskite oxide \( \text{Ba}_{1-x}\text{K}_x\text{BiO}_3 \) (BKBO) \([1,2]\) raises an interesting question of whether the layered structure and strong antiferromagnetic correlation in cuprates are essential for high-temperature superconductivity. In order to answer this question, it is important to find some common and distinct features in both systems. The band-structure calculations \([3]\) suggest that the bare density of states at Fermi level in BKBO is at least 3 times smaller than that in cuprates. Since tunneling and extensive oxygen-isotope experiments on BKBO \([4–8]\) seem to indicate that this material is a conventional phonon-mediated superconductor with an electron-phonon coupling constant \( \lambda \sim 1 \), one might argue that 100 K superconductivity in cuprates could be understood even within the conventional theory with \( \lambda \sim 3 \). If this were the case, the isotope effects in both cuprates and bismuthates would be similar. As a matter of fact, the oxygen-isotope exponent \( \alpha_O \) in BKBO has a maximum at optimal doping where \( T_c \) is the highest \([8]\), while \( \alpha_O \) in optimally-doped cuprates is the smallest \([3,2]\). Moreover, the isovalent substitution of Ca for Sr in the single-layer \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) system leads to a large decrease in \( T_c \), and to a large increase in \( \alpha_O \) \([3]\). Similarly, the isovalent substitution of Sr for Ba in \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) gives rise to a strong suppression of superconductivity from 93 K to 60 K \([14]\), and \( \alpha_O \) also increases with decreasing \( T_c \) \([15]\). If the pairing mechanism in bismuthates and cuprates were the same, this unusual \( T_c \) dependence of \( \alpha_O \) would also exist in bismuthates.

The isovalent substitution of Sr for Ba in \( \text{Ba}_{1-x}\text{K}_x\text{BiO}_3 \) cannot be realized using conventional solid-state reaction. Until recently, a new family of bismuth-oxide-based superconductor \( \text{Sr}_{1-x}\text{K}_x\text{BiO}_3 \) (SKBO) has been synthesized by a high pressure technique \([16]\). This material has a distorted perovskite structure and exhibits a superconductivity at about 12 K, which is much lower than that in \( \text{Ba}_{1-x}\text{K}_x\text{BiO}_3 \). It appears that the isovalent substitution effects on \( T_c \) in both \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) and \( \text{Ba}_{1-x}\text{K}_x\text{BiO}_3 \) are quite similar. Now the important question is whether \( \alpha_O \) in optimally-doped \( \text{Sr}_{1-x}\text{K}_x\text{BiO}_3 \) remains the same or increases substantially compared with the exponent in optimally-doped \( \text{Ba}_{1-x}\text{K}_x\text{BiO}_3 \). The clarification of this issue will provide important insight into the pairing mechanism of high temperature
superconductivity in both bismuthates and cuprates.

Here we report the oxygen-isotope effect in optimally-doped Sr$_{1-x}$K$_x$BiO$_3$ ($x = 0.6$) with $T_c = 12$ K. We found a large oxygen-isotope exponent $\alpha_O = 0.40(5)$, which is the same as for optimally doped Ba$_{1-x}$K$_x$BiO$_3$. The present isotope experiments clearly demonstrate that the conventional phonon-mediated mechanism is responsible for the superconductivity in bismuthates, and that the pairing mechanism in cuprates is unconventional.

The samples were synthesized by a high pressure technique [14]. First, the sample of Sr$_2$Bi$_2$O$_5$ was prepared by conventional solid state reaction using SrCO$_3$ and Bi$_2$O$_3$. The powders were mixed, ground thoroughly, and then fired in air at 700, 800, and 850 °C for 100 hours with several intermediate grindings. Stoichiometric amounts of Sr$_2$Bi$_2$O$_5$, KO$_2$ and Bi$_2$O$_3$ were mixed in a dry box (filled with argon) and packed into the gold capsules. The high pressure synthesis was carried out in a Belt-type apparatus at 2 GPa and 700 °C for 0.5 h. Oxygen isotope exchange was performed in a closed system and at 1 bar oxygen pressure. The $^{18}$O sample of pair I/pair II was prepared by annealing the powder sample at 350/375 °C for 100 h in an $^{18}$O$_2$ atmosphere (ISOTEC Inc. 97% $^{18}$O$_2$). The $^{16}$O control samples were annealed in the same condition as the $^{18}$O samples, but in an $^{16}$O$_2$ atmosphere.

The oxygen-isotope enrichments of the present samples cannot be reliably determined by the conventional method commonly used in the isotope experiments on the cuprates [17]. This is because the $^{18}$O sample can be decomposed during the back-exchange with the $^{16}$O isotope in the thermobalance. We, therefore, proposed a new method to determine the isotope content precisely. This method is based on the mass spectrometric determination of the produced water when the sample is reduced by hydrogen. The reduction was carried out on a Netzsch STA 405 thermoanalyzer connected to a Balzers QMG 420 quadrupole mass spectrometer (MS) by a heated (at about 200 °C) capillary. The mixed gas (20 vol% hydrogen and 80 vol% helium) was flowing through the thermoanalyzer with a rate of about 50 ml/min. The heating rate was 10 °C/min. The integrated intensities of the m/z = 20 ($^{18}$H$_2$O) and m/z = 18 ($^{16}$H$_2$O) signals were used for the determination of the ratio of evolved $^{16}$H$_2$O and $^{18}$H$_2$O. The decomposition of NaHCO$_3$ into H$_2$O and CO$_2$ was used to
calibrate the contribution of m/z = 20 (H\textsubscript{2}^{18}O) signal from the $^{16}$O sample. The details of the calibration were given in Ref. [18,19].

Fig. 1 shows the intensities of the mass spectrometric signals of m/z = 20 (H\textsubscript{2}^{18}O) and m/z = 18 (H\textsubscript{2}^{16}O) for the $^{16}$O sample (dash lines) and the $^{18}$O sample (solid lines) of pair I. The reduction of the oxides occurs in the temperature range 300-600 °C with two steps at about 430 and 530 °C for the $^{16}$O sample, and at about 440 and 520 °C for the $^{18}$O sample. From the integrated intensities of m/z = 20 (H\textsubscript{2}^{18}O) and m/z = 18 (H\textsubscript{2}^{16}O) signals, we calculated that the $^{18}$O sample of pair I contains 60(2)% $^{18}$O isotope. The $^{18}$O sample of pair II contains $\sim$80% $^{18}$O isotope.

The isotope-exchanged samples were characterized by x-ray diffraction technique using a STADI-P diffractometer equipped with a mini-PSD detector and a Ge monochromator on the primary beam. The diffraction patterns were recorded in the $2\theta = 10$-90° range in a transmission mode by rotating the sample. Fig. 2 shows the x-ray diffraction pattern of the $^{18}$O sample of pair I. All peaks can be indexed on the basis of a distorted perovskite cell with lattice parameters $a \approx b \approx \sqrt{2}a_p$ and $c \approx 2a_p$, where $a_p$ refers to the ideal cubic perovskite cell ($a_p \sim 4$ Å). No impurity phase can be seen from the spectrum. On the other hand, the samples (pair II) annealed at 375 °C contain small amount of impurity phase, namely, SrBi\textsubscript{2}O\textsubscript{4} (about 5%).

For magnetic measurements, we pressed the samples into pellets with a diameter of 3 mm and sealed them in respective quartz tubes. Magnetization of the samples was measured using a SQUID magnetometer in a magnetic field of 1 mT. Measurements were carried out in field cooled condition, and the data were corrected upon warming.

Fig. 3 shows the field-cooled susceptibility of the $^{16}$O and $^{18}$O samples of pair I over 2-15 K. It is apparent that $T_c$ for the $^{18}$O is lower than for the $^{16}$O sample. The $T_c$ (diamagnetic onset temperature) of the $^{16}$O sample is about 11.5 K, in good agreement with the value reported in Ref. [16]. Furthermore, the low-temperature susceptibility for the $^{18}$O sample is lower than for the $^{16}$O sample by about 7(2)%. We are not sure that this is a real effect. The isotope back-exchange is required to clarify this, but we were unable to do the back-exchange
due to the fact that a further increase of the annealing time will lead to a decomposition of the sample.

In Fig. 4, we plot the normalized magnetizations for the $^{16}$O and $^{18}$O samples of pair I and pair II. One can see that the transition curves are parallel for the $^{16}$O and $^{18}$O samples of pair I (Fig. 4a), while this is not the case for pair II (Fig. 4b). In order to eliminate effects due to possible differences in demagnetization factor, particle size, and superconducting fraction of the magnetization data extended to the base line at zero magnetization. The isotope shift is $0.32(2)$ K for pair I, and $0.50(4)$ K for pair II. The isotope effect exponent $\alpha_O$ was calculated from the definition $\alpha_O = -d\ln T_c/d\ln M_O$, where $M_O$ is the atomic mass of the oxygen-isotopes corrected for the incomplete exchange. We find that $\alpha_O = 0.37(3)$ for pair I, and $0.42(4)$ for pair II. Both the values are very close to the exponent found for Ba$_{1-x}$K$_x$BiO$_3$ with the highest $T_c$.

The most striking feature we found for the bismuthate superconductors is that the oxygen-isotope exponent reaches a maximum at optimal doping, and that the maximum value is close to 0.5, independent of $T_c$. This is in sharp contrast to the isotope effects in cuprates where $\alpha_O$ becomes very small at optimal doping. Moreover, the isovalent substitution of Ca for Sr in La$_{2-x}$Sr$_x$CuO$_4$ system leads to a large decrease in $T_c$, and to a large increase in $\alpha_O$. Similar result has been found for the isovalent substitution of Sr for Ba in YBa$_2$Cu$_3$O$_7$. The $T_c$ dependence of $\alpha_O$ for optimally-doped bismuthates and cuprates are very different as shown in Fig. 5. It is remarkable that $\alpha_O$ in bismuthates is nearly independent of $T_c$, whereas $\alpha_O$ in cuprates increases linearly with decreasing $T_c$. The very distinctive isotope effects observed in the bismuthates and cuprates strongly suggest that the microscopic superconducting mechanisms in the two systems should be different.

It is known that the isotope exponent in conventional phonon-mediated superconductors is close to 0.5, and nearly independent of $T_c$. The fact that the isotope exponent in optimally-doped bismuthates is also close to 0.5 and independent of $T_c$ (see Fig. 5) provides strong evidence for the conventional phonon-mediated pairing mechanism in this system.
The very different isotope effects observed in cuprates indicate that the microscopic pairing mechanism in this system should be unconventional. The unconventional pairing mechanism in cuprates should be related to the unique features such as two-dimensionality, antiferromagnetic fluctuations and polaronic effects. Any feasible theories for high-temperature superconductivity in cuprates must be able to explain the unusual doping and $T_c$ dependencies of the oxygen-isotope exponent.

In summary, oxygen-isotope effect has been investigated in a recently discovered superconductor Sr$_{1-x}$K$_x$BiO$_3$. This material can be synthesized by a high pressure technique. At an optimal doping of $x = 0.6$, the compound exhibits superconductivity at about 12 K. Upon replacing $^{16}$O with $^{18}$O by 60-80%, the $T_c$ of the sample is shifted down by 0.32-0.50 K, corresponding to an isotope exponent of $\alpha_O = 0.40(5)$. This isotope exponent is very close to that for a similar bismuthate superconductor Ba$_{1-x}$K$_x$BiO$_3$ with $T_c = 30$ K. The present results clearly suggest that bismuthates should belong to conventional phonon-mediated superconductors while cuprates might be unconventional superconductors.

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FIG. 1. The intensities of the mass spectrometric signals of m/z = 20 (H$_2^{18}$O) and m/z = 18 (H$_2^{16}$O) for the $^{16}$O sample (dash lines) and the $^{18}$O sample (solid lines) of pair I. From the integrated intensities of the signals, we find that the $^{18}$O sample contains 60(2)% $^{18}$O isotope.
FIG. 2. X-ray diffraction pattern of the $^{18}$O sample of pair I. All peaks can be indexed on the basis of a distorted perovskite cell with lattice parameters $a \simeq b \simeq \sqrt{2}a_p$ and $c \simeq 2a_p$, where $a_p$ refers to the ideal cubic perovskite cell ($a_p \sim 4$ Å). No impurity phase can be seen from the spectrum.
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FIG. 5. \( T_c \) dependence of the oxygen-isotope exponent \( \alpha_O \) for optimally-doped bismuthates and cuprates. The data for \( \text{Ba}_{1-x}\text{K}_x\text{BiO}_3 \) are from Ref. [6,8], and the data for the cuprates are taken from Ref. [10,15]. The data for \( \text{Sr}_{1-x}\text{K}_x\text{BiO}_3 \) \((T_c = 12 \text{ K})\) are from this work.