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Large oxygen-isotope effect in $Sr_{0.4}K_{0.6}BiO_3$: Evidence for phonon-mediated superconductivity

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The 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 $Ba_{1-x}K_xBiO_3$ with $T_c = 30$ K. The very distinctive doping and T_c dependencies of α_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 $Ba_{1-x}K_xBiO_3$ (BKBO) (Refs. 1 and 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 the Fermi level in BKBO is at least three times smaller than that in cuprates. Since tunneling and extensive oxygen-isotope experiments on BKBO (Refs. 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 α_O in BKBO has a maximum at optimal doping where T_c is the highest,[8] while α_O in optimally-doped cuprates is the smallest.[9–12] Moreover, the isovalent substitution of Ca for Sr in the single-layer $La_{2-x}Sr_xCuO_4$ system leads to a large decrease in T_c, and to a large increase in α_O.[13] Similarly, the isovalent substitution of Sr for Ba in $YBa_2Cu_3O_7$ gives rise to a strong suppression of superconductivity from 93 to 60 K,[14] and α_O also increases with decreasing T_c.[15] If the pairing mechanism in bismuthates and cuprates was the same, this unusual T_c dependence of α_O would also exist in bismuthates.

The isovalent substitution of Sr for Ba in $Ba_{1-x}K_xBiO_3$ cannot be realized using conventional solid-state reaction. Until recently, an additional family of bismuth-oxide-based superconductor $Sr_{1-x}K_xBiO_3$ (SKBO) has been synthesized by a high-pressure technique.[16] This material has a distorted perovskite structure and exhibits superconductivity at about 12 K, which is much lower than that in $Ba_{1-x}K_xBiO_3$. It appears that the isovalent substitution effects on T_c in both $YBa_2Cu_3O_7$ and $Ba_{1-x}K_xBiO_3$ are quite similar. Now the important question is whether α_O in optimally doped $Sr_{1-x}K_xBiO_3$ remains the same or increases substantially compared with the exponent in optimally doped $Ba_{1-x}K_xBiO_3$. 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 $Sr_{1-x}K_xBiO_3$ ($x = 0.6$) 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 $Ba_{1-x}K_xBiO_3$. 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.[16] First, the sample of $Sr_2Bi_2O_5$ was prepared by conventional solid-state reaction using $SrCO_3$ and Bi_2O_3. The powders were mixed, ground thoroughly, and then fired in air at 700, 800, and 850 °C for 100 h with several intermediate grindings. Stoichiometric amounts of $Sr_2Bi_2O_5$, KO_2, and Bi_2O_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]

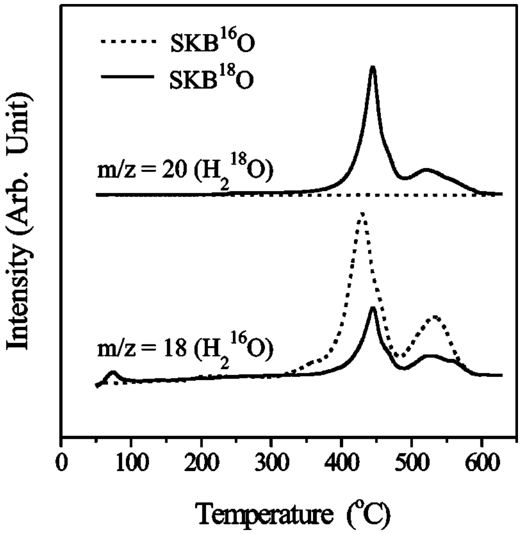


FIG. 1. The intensities of the mass spectrometric signals of $m/z=20$ ($H_2{}^{18}O$) and $m/z=18$ ($H_2{}^{16}O$) for the ^{16}O sample (dash lines) and the ^{18}O sample (solid lines) of pair I. From the integrated intensities of the signals, we find that the ^{18}O sample contains 60(2)% ^{18}O isotope.

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 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 $m/z=20$ ($H_2{}^{18}O$) and $m/z=18$ ($H_2{}^{16}O$) signals were used for the determination of the ratio of evolved $H_2{}^{16}O$ and $H_2{}^{18}O$. The decomposition of $NaHCO_3$ into H_2O and CO_2 was used to calibrate the contribution of the $m/z=20$ ($H_2{}^{18}O$) signal from the ^{16}O sample. The details of the calibration were given in Refs. 18 and 19.

Figure 1 shows 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. 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 the $m/z=20$ ($H_2{}^{18}O$) and $m/z=18$ ($H_2{}^{16}O$) 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 ~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. Figure 2 shows the x-ray-diffraction pattern of the ^{18}O sample of pair I. The x-ray pattern for the isotope-exchanged sample is the same as that for a single-phase sample which was shown to have a tetragonal structure with $a=5.9418$ Å and $b=8.4394$ Å.[16] On the other hand, the samples (pair II) annealed at 375 °C contain a small amount of impurity phase, namely, $SrBi_2O_4$ (about 5%).

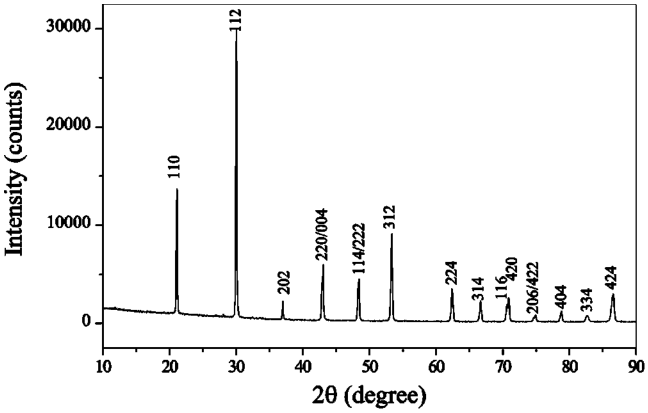
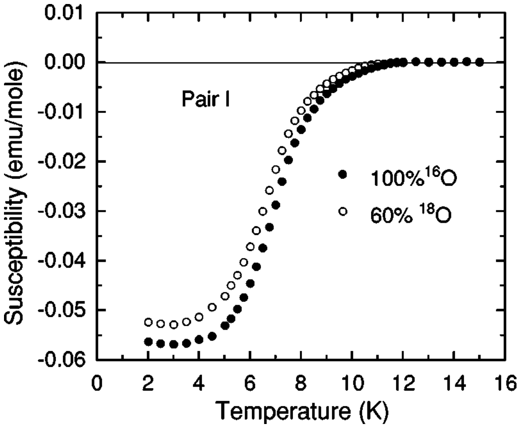


FIG. 2. X-ray-diffraction pattern of the ^{18}O sample of pair I. The x-ray pattern for the isotope-exchanged sample is the same as that for a single-phase sample which was shown to have a tetragonal structure with $a=5.9418$ Å and $b=8.4394$ Å (Ref. 16). No impurity phase can be seen from the spectrum.

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 superconducting quantum interference device magnetometer in a magnetic field of 1 mT. Measurements were carried out in field-cooled condition, and the data were corrected upon warming.

Figure 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.



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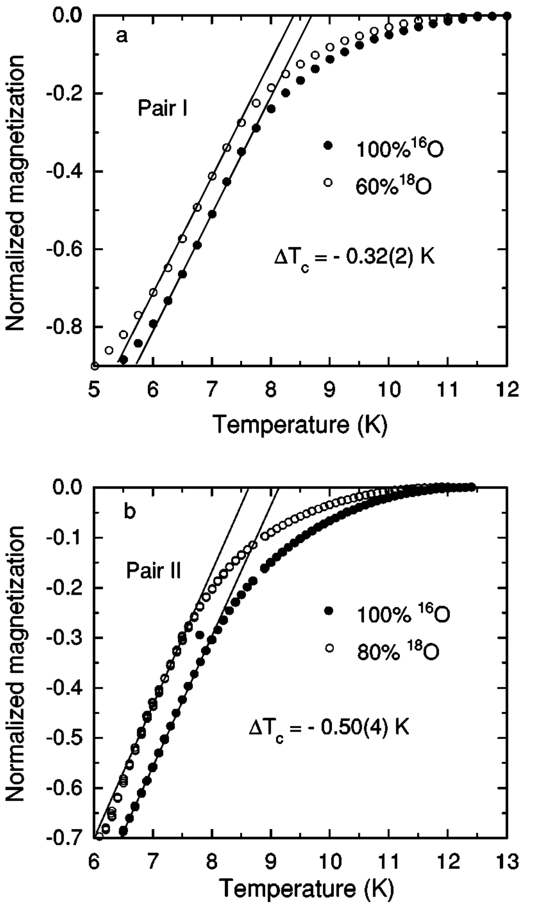

FIG. 4. The normalized magnetizations for the ^{16}O and ^{18}O samples of pair I and pair II. The isotope shifts of T_c are determined from the linear portion of the magnetization data extended to the base line at zero magnetization.

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. 4(a)], while this is not the case for pair II [Fig. 4(b)]. In order to eliminate effects due to possible differences in demagnetization factor, particle size, and superconducting fraction of two isotope samples, the isotope shifts of T_c are determined from the linear portion 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 α_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 $Ba_{1-x}K_xBiO_3$ with the highest T_c.[6,8]

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 α_O becomes very small at optimal doping. Moreover, the isovalent substitution of Ca for Sr in the $La_{2-x}Sr_xCuO_4$ system leads to a large decrease in T_c, and to a large increase in α_O.[13] A similar result has been found for the isovalent substitution of Sr for Ba in $YBa_2Cu_3O_7$.[15] The T_c dependence of α_O for optimally doped bismuthates and cuprates is very different as shown in Fig. 5. It is remarkable that α_O in bismuthates is nearly independent of T_c, whereas α_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.

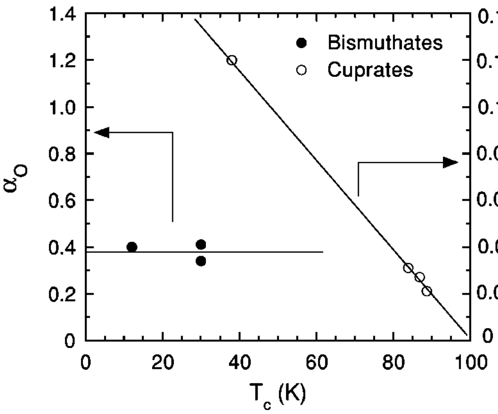

FIG. 5. T_c dependence of the oxygen-isotope exponent α_O for optimally doped bismuthates and cuprates. The data for $Ba_{1-x}K_xBiO_3$ are from Refs. 6 and 8, and the data for the cuprates are taken from Refs. 10 and 15. The data for $Sr_{1-x}K_xBiO_3$ ($T_c = 12$ K) are from this work.

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, the oxygen-isotope effect has been investigated in a recently discovered superconductor $Sr_{1-x}K_xBiO_3$. 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 $Ba_{1-x}K_xBiO_3$ 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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