

Composition dependence of the oxygen isotope effect in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$: Evidence for oxygen-mass dependence of the coupling constant

Guo-meng Zhao and Donald E. Morris

Morris Research Inc., 1918 University Avenue, Berkeley, California 94704

(Received 24 January 1995)

We report measurements of the oxygen isotope effect and temperature dependence of the penetration depth for high- T_c superconductors $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with $x = 0.45, 0.375, \text{ and } 0.36$. We find that, with the decrease of the K content, both the oxygen isotope exponent $\alpha_O = -d \ln T_c / d \ln M_O$ and reduced energy gap $\delta = 2\Delta(0)/k_B T_c$ increase: $\alpha_O = 0.21 \pm 0.02, \delta = 4.0 \pm 0.2$ for $x = 0.45$; $\alpha_O = 0.26 \pm 0.02, \delta = 4.5 \pm 0.2$ for $x = 0.375$; $\alpha_O = 0.34 \pm 0.03, \delta = 4.8 \pm 0.2$ for $x = 0.36$. Our results can be explained by a picture in which the electron-phonon coupling constant is oxygen-mass dependent due to the anharmonicity of phonon modes and/or the breakdown of the Migdal adiabatic approximation.

Whether the conventional phonon-mediated mechanism is responsible for the high- T_c superconductivity in the oxide superconductor $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (BKBO) is still an open question. One way to address this question is the isotope-effect experiment. For conventional (BCS) superconductors containing a single type of atom, the isotope-effect exponent $\alpha = -d \ln T_c / d \ln M \sim 0.5$, if one assumes no anharmonicity for the phonon modes and no Coulomb interaction.^{1,2} The anharmonicity of the phonon modes and Coulomb interaction will significantly modify the isotope effect in the weak-coupling limit.^{1,2} In the strong-coupling limit, however, the modification is small.^{1,2}

While Batlogg *et al.*³ reported a reduced oxygen isotope effect ($\alpha_O \sim 0.2$) in BKBO, the other two groups (Hinks *et al.*⁴ and Kondoh *et al.*⁵) observed a large oxygen isotope effect ($\alpha_O \sim 0.3-0.4$). It appears that the result reported by Batlogg *et al.* looks convincing for two reasons. One is that the isotope-exchange temperature is low ($\sim 350^\circ\text{C}$) so that the loss of potassium is not expected. The second reason is that the observed oxygen isotope effect for BKBO is similar to that for a similar compound $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ [$\alpha_O = 0.22$ (Ref. 3)]. On the other hand, we cannot find anything wrong in Hinks *et al.* experiment. The question is why these results appear to conflict. One possible explanation to this apparent contradiction is that the oxygen isotope effect in this system is composition or sample dependent.

Here we report measurements of the oxygen isotope effect and temperature dependence of penetration depth for high- T_c superconductors $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with $x = 0.45, 0.375, \text{ and } 0.36$. We find that, with decreasing K content, both the oxygen isotope exponent $\alpha_O = -d \ln T_c / d \ln M_O$ and reduced energy gap $\delta = 2\Delta(0)/k_B T_c$ increase: $\alpha_O = 0.21 \pm 0.02, \delta = 4.0 \pm 0.2$ for $x = 0.45$; $\alpha_O = 0.26 \pm 0.02, \delta = 4.5 \pm 0.2$ for $x = 0.375$; $\alpha_O = 0.34 \pm 0.03, \delta = 4.8 \pm 0.2$ for $x = 0.36$. Our results can be explained by a picture in which the electron-phonon coupling constant is oxygen mass dependent due to the anharmonicity of phonon modes and/or the breakdown of the Migdal adiabatic approximation.

The isotope-exchange experiments were carried out in two parallel quartz tubes separated by about 2 cm.⁶ The

starting materials for the ^{16}O and ^{18}O samples were taken from the same well-ground powder mixtures of high-purity K_2CO_3 (99.995%), BaCO_3 (99.999%), and Bi_2O_3 (99.999%), and had the same weight (~ 150 mg). The two samples were wrapped in gold foils (which had similar size) and placed inside respective quartz tubes for the ^{16}O and ^{18}O treatment. The powder mixtures were reacted in vacuum at 720°C for 2 h and then quickly cooled to 100°C in ~ 3 min. Throughout the reaction, the system was continuously pumped to keep a high vacuum (the ^{16}O and ^{18}O sides of the diffusion apparatus were connected together and had the same vacuum). Then the ^{16}O side was filled with $^{16}\text{O}_2$ gas (99.993% ^{16}O , 0.005% ^{17}O , 0.002% ^{18}O , CO < 14 ppm, CO_2 < 7 ppm, CH_4 < 5 ppm, H < 39 ppm, He < 13 ppm, and N < 18 ppm), and the ^{18}O side was filled with $^{18}\text{O}_2$ gas (96.9% ^{18}O , 2.6% ^{16}O , 0.5% ^{17}O , CO < 18 ppm, CO_2 < 18 ppm, CH_4 < 7 ppm, N < 21 ppm, H < 18 ppm, and He < 15 ppm). The oxygen pressure for the ^{16}O and ^{18}O sides was the same within $\pm 3\%$. The furnace was then heated to 450°C at $5^\circ\text{C}/\text{min}$, held for 0.5 h, and cooled to room temperature at $5^\circ\text{C}/\text{min}$. This technique prevents the samples from being exposed to the atmosphere throughout the preparation. X-ray diffraction results indicate that a large portion of the samples ($> 85\%$) is the superconducting phase with sharp diffraction peaks (a clear Cu $K\alpha 1$ -Cu $K\alpha 2$ splitting is observed above a diffraction angle of 60°), and $\sim 5-15\%$ portion of the samples are K poor and nonsuperconductive. As the K content increases, the percentage of the nonsuperconducting phase increases slightly. From the measured lattice constants, we find that the K content x of the superconducting phase is close to the starting composition, while the x of the nonsuperconducting phase is ~ 0.2 lower than the starting composition. The thermogravimetric analysis shows that the ^{18}O samples have $\sim 80 \pm 5\%$ ^{18}O , in excellent agreement with Hinks *et al.* observation⁴ that a single cycle of oxygen isotope exchange (as in our case) will give an 85% exchange fraction.

The susceptibility was measured with a Quantum Design SQUID magnetometer. The powder samples of ~ 130 mg (without further grinding) were placed in a

gelatin capsule. The field-cooled, measured-on-warming susceptibility (FCW) was measured in a field of $\sim 5.0 \pm 0.3$ Oe, which was calibrated by measuring the field dependence of magnetization for the $x = 0.36$ sample at 5 K, and kept unchanged throughout the whole series of measurements. The samples were cooled in the field from 35 to 2 K. The data were collected upon warming.

The reduced energy gap $2\Delta(0)/k_B T_c$ can be determined by the temperature dependence of penetration depth $\lambda(t)$ at low temperatures which, for an s -wave superconductor, follows⁷

$$\Delta\lambda(t) \equiv \lambda(t) - \lambda(0) = \lambda(0)(\beta\pi/2)^{1/2} t^{-1/2} \exp(-\beta/t), \quad (1)$$

where $t = T/T_c < 0.5$ and $\beta = \Delta(0)/k_B T_c$. For fine-grained, decoupled powder samples, $\Delta\lambda(t)$ can be evaluated from the temperature dependence of the Meissner fraction $f(t) = f(\lambda(t), \{r\})$, where $\{r\}$ represents any particle-radius distribution. At low temperatures where $\Delta\lambda(t)/\lambda(0) \ll 1$, we can make a Taylor expansion for $f(t) = f(\lambda(t), \{r\})$, leading to

$$-\Delta f(t)/f(0) = B\Delta\lambda(t)/\lambda(0), \quad (2)$$

where $B = -[\lambda(0)/f(0)][\partial f(\lambda(t), \{r\})/\partial \lambda(t)]_{t=0}$, which depends on $\lambda(0)$ and the particle size distribution $\{r\}$. Equation (2) is a general expression which is valid for any particle-radius distribution as long as $\Delta\lambda(t)/\lambda(0) \ll 1$, which is always satisfied for $t < 0.5$ as seen from Eq. (1).

It is known that the measured FCW susceptibility $\chi(t)$ is the sum of trapped susceptibility $m(t)$ (due to flux-pinning and surface-barrier effects), and the Meissner susceptibility $f(t)$. For the FCW measurement, $m(t)$ has the weakest temperature dependence and is nearly temperature independent below $t \sim 0.5$, as shown by Clem and Hao.⁸ We can write $\chi(t) = m(t) + f(t) = m(t) + f(0) + \Delta f(t)$. For s -wave superconductors, the penetration depth $\lambda(t)$ is nearly temperature independent below $t = 0.1$, $\beta = 0.18$ according to Eq. (1). In this temperature range ($t < 0.18$), both $\Delta\lambda(t)$ and $\Delta f(t)$ are negligible, and $m(t) + f(0) = \chi(t)$. For the samples studied here, we find $\chi(t)$ is nearly temperature independent below $t = 0.18$. This implies that the temperature dependence of the trapped susceptibility in our samples can be neglected at low temperatures.

In Fig. 1, we show the temperature dependence of

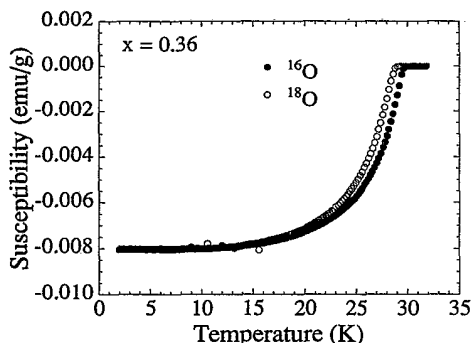


FIG. 1. The temperature dependence of FCW susceptibility for the ^{16}O and ^{18}O samples of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with $x = 0.36$. The measuring magnetic field was calibrated and determined to be 5.0 ± 0.3 Oe.

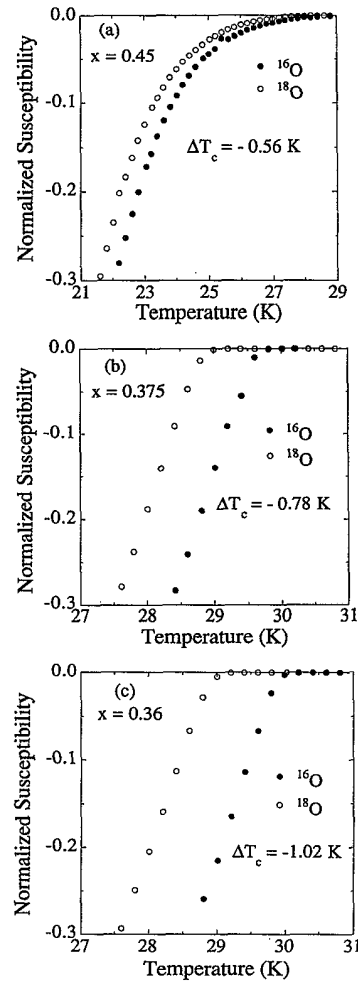


FIG. 2. The normalized susceptibility near T_c for the ^{16}O and ^{18}O samples of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with (a) $x = 0.45$, (b) $x = 0.375$, and (c) $x = 0.36$. At low temperatures, the Meissner fractions of the ^{16}O and ^{18}O samples are the same within $\pm 3\%$ in all the cases. The Meissner fractions at 5 K are determined to be $\sim 47 \pm 5\%$ with a correction of demagnetization factor of $\frac{1}{3}$. The ^{18}O samples have $\sim 80 \pm 5\%$ ^{18}O .

FCW susceptibility for the ^{16}O and ^{18}O samples of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with $x = 0.36$. At low temperatures, the Meissner fractions for the ^{16}O and ^{18}O samples are the same within $\pm 1.5\%$. With a correction of demagnetization factor of $\frac{1}{3}$, we evaluate the Meissner fraction $f(0) \sim 50\%$.

Figures 2(a)–2(c) show the normalized susceptibility (normalized to the susceptibility at 2 K) near T_c for the ^{16}O and ^{18}O samples of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with $x = 0.45$, 0.375 , and 0.36 , respectively. At low temperatures, the Meissner fractions of the ^{16}O and ^{18}O samples are the same within $\pm 3\%$ in all the cases, and have the magnitudes of $\sim 47 \pm 5\%$ with a correction of demagnetization factor of $\frac{1}{3}$. The diamagnetic shielding fraction is $\sim 10\%$ larger than the Meissner fraction, implying a small flux trapping. The observation that the Meissner fractions for the ^{16}O and ^{18}O samples are nearly the same indicates that the members of the sample pairs are similar in grain size, demagnetization factor, and composition. Further-

more, the diamagnetic transitions for the ^{16}O and ^{18}O samples are parallel, so the isotope shifts measured at different places along the transition curves are the same within $\pm 4\%$.

For the $x=0.45$ sample, the T_c and transition width are similar to those reported by Batlogg *et al.*³ The oxygen isotope-effect exponent $\alpha_O = -d \ln T_c / d \ln M_O$ is determined to be $\alpha_O = 0.20 \pm 0.02$ if we take $\Delta T_c = -1.35$ K, $T_c = 28$ K (onset T_c), and $\Delta M_O / M_O = 10 \pm 1\%$. Our result is in excellent agreement with that observed by Batlogg *et al.* On the other hand, the samples with $x=0.375$ and 0.36 have a very sharp diamagnetic transition, indicative of excellent sample homogeneity. The oxygen isotope-effect exponent α_O is evaluated to be 0.26 ± 0.02 for $x=0.375$, and 0.34 ± 0.03 for $x=0.36$ by

taking $T_c = 29.6$ K for $x=0.375$ and 29.9 K for $x=0.36$. The oxygen isotope exponent ($\alpha_O = 0.34$) for the $x=0.36$ sample is similar to those reported by Hinks *et al.* [$\alpha_O = 0.36$ evaluated from $T_c = 29.6$ K, $\Delta T_c = -1.35$ K and $\Delta M_O / M_O = 12.5\%$ (Ref. 4)] and Kondoh *et al.* [$\alpha_O = 0.35$ (Ref. 5)].

In Figs. 3(a)–3(c), we show the results of $-\Delta f(t)/f(0)$ vs t for $x=0.45$, 0.375 , and 0.36 samples, respectively. The temperature dependence of $-\Delta f(t)/f(0)$ can be fitted by $1.6t^{-1/2}\exp(-2.00/t)$ for the $x=0.45$ sample; by $1.8t^{-1/2}\exp(-2.25/t)$ for the $x=0.375$ sample; and by $2.0t^{-1/2}\exp(-2.38/t)$ for the $x=0.36$ samples (see solid dots in Fig. 3). Comparing these results with Eqs. (1) and (2), we find $\beta = \Delta(0)/k_B T_c = 2.00$ for $x=0.45$, $\beta = 2.25$ for $x=0.375$, and $\beta = 2.38$ for $x=0.36$. So the reduced energy gap is $\delta = 2\Delta(0)/k_B T_c = 4.0 \pm 0.2$ for $x=0.45$, $\delta = 4.5 \pm 0.2$ for $x=0.375$, and $\delta = 4.8 \pm 0.2$ for $x=0.36$.

Carbotte¹ has shown that the reduced energy gap is a unique function of the electron-phonon coupling constant λ_{e-ph} and Coulomb pseudopotential μ^* when $\lambda_{e-ph} < 2$. If we take $\mu^* = 0.1$ for BKBO, then we can estimate λ_{e-ph} to be $\sim 1.00 \pm 0.10$ for $x=0.45$, 1.45 ± 0.10 for $x=0.375$, and 1.80 ± 0.10 for $x=0.36$ from the data summarized in Ref. 1. For the $x=0.36$ samples, Affronte *et al.* have estimated $\lambda_{e-ph} \sim 1.7$ – 2.1 from their resistivity data,⁹ in agreement with our result. These results consistently suggest that the coupling indeed becomes stronger as the composition closes to the boundary of insulating and superconducting phases [$x \sim 0.35$ (Ref. 10)].

The above results indicate that both oxygen isotope exponents and coupling constants increase when the K content is reduced toward the phase boundary. Since the transition temperature in BKBO depends on the oxygen and K contents as shown by Idemoto *et al.*,¹¹ the composition dependence of the oxygen isotope effect may be explained as due to the differences in oxygen and/or K contents of the ^{16}O and ^{18}O samples. Since Batlogg *et al.*³ have carried out the oxygen diffusion at a temperature less than 350°C , the loss of potassium would not be expected and the ^{16}O and ^{18}O samples would have the same K content. The same oxygen isotope exponent was found in our samples which were diffused at 450°C , implying that the K contents in our ^{16}O and ^{18}O samples were also the same even if the loss of potassium was likely. It is also possible that the ^{16}O and ^{18}O samples may have slightly different oxygen contents. However, the reversibility of the transition temperature upon back exchange⁴ suggests that the ^{16}O and ^{18}O samples may have the same oxygen content. Since our samples with $x=0.36$ and 0.375 have the transition temperatures close to the highest one (optimally doped), any small difference in oxygen contents of the ^{16}O and ^{18}O samples will not lead to an observable difference in T_c . Moreover, we have shown that a similar diffusion procedure for La_2CuO_4 and $\text{Gd}_{1.9}\text{Ce}_{0.1}\text{CuO}_4$ systems causes the same oxygen content in the ^{16}O and ^{18}O samples.¹²

The close correlation of the oxygen isotope exponent with the reduced energy gap (or the coupling constant) leads us to suggest an unconventional interpretation to the observed results. As shown below, the isotope ex-

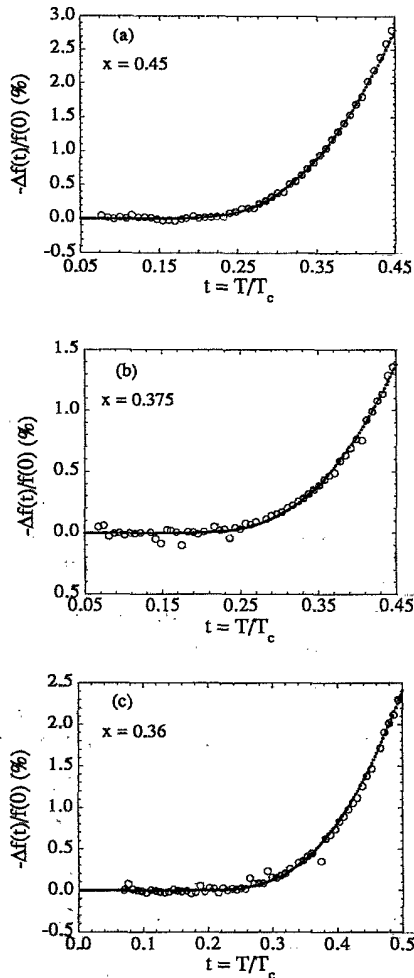


FIG. 3. The result of $-\Delta f(t)/f(0)$ vs t for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with (a) $x=0.45$, (b) $x=0.375$, and (c) $x=0.36$. The solid dots are for the fitted curves: (a) $-\Delta f(t)/f(0) = 1.6t^{-1/2}\exp(-2.00/t)$ for $x=0.45$; (b) $-\Delta f(t)/f(0) = 1.8t^{-1/2}\exp(-2.25/t)$ for $x=0.375$; (c) $-\Delta f(t)/f(0) = 2.0t^{-1/2}\exp(-2.38/t)$ for $x=0.36$. The reduced energy gap is determined as 4.0 ± 0.2 for $x=0.45$, 4.5 ± 0.2 for $x=0.375$, and 4.8 ± 0.2 for $x=0.36$.

ponent will strongly depend on the electron-phonon coupling constant λ_{e-ph} if λ_{e-ph} is ion-mass dependent.

For conventional superconductors, the superconducting transition temperature T_c can be expressed as $T_c = T_c(\lambda_{e-ph}, \Omega, \mu^*)$, where Ω represents an average of phonon spectrum. Then the partial isotope-effect exponent ($\alpha = -d \ln T_c / d \ln M$) is given by

$$\begin{aligned} \alpha = & -(d \ln T_c / d \ln \Omega)(d \ln \Omega / d \ln M) \\ & -(d \ln T_c / d \ln \mu^*)(d \ln \mu^* / d \ln M) \\ & -(d \ln T_c / d \ln \lambda_{e-ph})(d \ln \lambda_{e-ph} / d \ln M). \end{aligned} \quad (3)$$

For conventional superconductors, one has $\alpha_\lambda = -d \ln \lambda_{e-ph} / d \ln M \sim 0$, $\alpha_\Omega = -d \ln \Omega / d \ln M \sim 0.5$ (for metals with a single atom), and $\alpha \sim 0.5$. However, Pickett, Cohen, and Krakauer¹³ have shown that $\alpha_\lambda \neq 0$ if there is a strong anharmonicity of phonon modes. The strong anharmonicity of phonon modes makes the average electronic structure or $N(E_F)$ (the average density of states) dependent on the ionic mass.¹³ Using $\lambda_{e-ph} = N(E_F) \langle I \rangle^2 / M \Omega^2$ [where $\langle I \rangle$ is the average matrix element of the electron-phonon interaction (Ref. 15)], we have

$$\alpha_\lambda = -[d \ln N(E_F) + d \ln (\langle I \rangle^2) - d \ln (M \Omega^2)] / d \ln M. \quad (4)$$

Equation (4) indicates that the ionic-mass dependence of $M \Omega^2$ will contribute to α_λ . Crespi, Cohen, and Penn² have shown that the anharmonicity of phonon modes will make $M \Omega^2$ depend on the ionic mass.

An alternative origin for the ionic-mass dependence of $N(E_F)$ could be the breakdown of the Migdal adiabatic approximation. With the aid of a generalized Ward's identity for the electron-phonon vertex $\Gamma(p, q)$, Engelesberg and Schrieffer¹⁴ showed that the Migdal approxima-

$$\alpha = \alpha_\Omega - [1.04\alpha_\Omega(1 + \lambda_{e-ph})(1 + 0.62\lambda_{e-ph})\mu^{*2} - 1.04\lambda_{e-ph}(1 + 0.38\mu^*)\alpha_\lambda] / [\lambda_{e-ph} - \mu^*(1 + 0.62\lambda_{e-ph})]^2. \quad (5)$$

In Fig. 4, we plot the curve of Eq. (5) with $\alpha_\Omega = 0.5$, $\alpha_\lambda = -0.20$, and $\mu^* = 0.1$. The open circles along with the error bars represent our experimental results.

Our fitting parameters ($\alpha_\Omega = 0.5$, $\alpha_\lambda = -0.20$ for oxygen) seem to indicate that only the phonons related to oxygen contribute to the pairing. However, the combined results of tunneling spectra¹⁶ and molecular-dynamics simulation¹⁷ suggest that the phonons (~ 15 meV) related to the Bi ion also have a small contribution to the pairing interaction, so that $\alpha_\Omega < 0.5$. Because McMillan's T_c formula is not very accurate when $\lambda_{e-ph} > 1.5$, and there are limited data points, the fitting parameters will have a substantial error.

¹J. P. Carbotte, Rev. Mod. Phys. **62**, 1027 (1990).

²V. H. Crespi, M. L. Cohen, and D. R. Penn, Phys. Rev. B **43**, 12 921 (1991).

³B. Batlogg *et al.*, Phys. Rev. Lett. **61**, 1670 (1988).

⁴D. G. Hinks *et al.*, Nature **335**, 419 (1988); Physica C **162-164**, 1405 (1989).

⁵S. Kondoh *et al.*, Physica C **157**, 469 (1989).

⁶J. H. Nickel, D. E. Morris, and J. W. Ager, III, Phys. Rev. Lett. **70**, 81 (1993).

⁷J. P. Turneare *et al.*, J. Supercond. **4**, 341 (1991).

⁸J. R. Clem and Z. D. Hao, Phys. Rev. B **48**, 13 774 (1993).

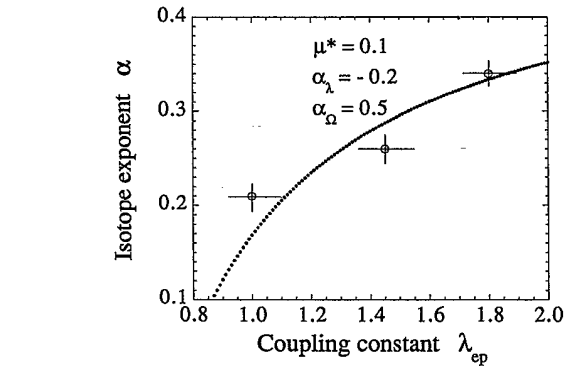


FIG. 4. The dependence of isotope effects on the coupling constant. The solid dots represent the curve of Eq. (5) (see text) with $\alpha_\Omega = 0.5$, $\alpha_\lambda = -0.20$, and $\mu^* = 0.1$. The open circles along with the error bars represent our experimental results. The same parameters also agree with the results reported by Hinks *et al.* [$\alpha_O \sim 0.40 \pm 0.03$ and $2\Delta(0)/k_B T_c \sim 5.3 - 5.5$ (Ref. 4)].

tion [i.e., $\Gamma(p, q) \sim 1$] does not hold when the phonon's phase velocity is of the order or greater than the Fermi velocity. For compounds, there exist long-wavelength ($q \rightarrow 0$) optical phonons which have the phase velocity $\Omega/q \rightarrow \infty$, so that the Migdal approximation breaks down. In this case, $\Gamma(p, q=0) \sim 1 + g^2 N_b(E_F) / (\Omega^2 - \epsilon_p^2) \sim 2$,¹⁴ where g is the matrix element of electron-phonon interaction and $N_b(E_F)$ is the density of states assuming the rigid lattice. The real density of states $N(E_F)$ will depend on the average of $\Gamma(p, q=0)$ which is ionic mass dependent.

Regardless of the origin of α_λ , we can deduce a general expression for a partial isotope exponent using McMillan's T_c formula,¹⁵

In conclusion, we have measured the oxygen isotope effect and temperature dependence of the penetration depth for high- T_c superconductors $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with $x = 0.45, 0.375$, and 0.36 . We find that with the decrease of K content both the oxygen isotope exponent α_O and the reduced energy gap $2\Delta(0)/k_B T_c$ increase. Our results can be explained by a picture in which the electron-phonon coupling constant is oxygen mass dependent due to the anharmonicity of phonon modes and/or the breakdown of Migdal adiabatic approximation.

The authors thank B. Batlogg for valuable comments and suggestions on this paper.

⁹M. Affronte *et al.*, Phys. Rev. B **49**, 3502 (1994).

¹⁰Shiyou Pei *et al.*, Phys. Rev. B **41**, 4126 (1990).

¹¹Y. Idemoto *et al.*, Physica C **222**, 257 (1994).

¹²Guo-meng Zhao *et al.*, Phys. Rev. B **50**, 4112 (1994).

¹³W. E. Pickett, R. E. Cohen, and H. Krakauer, Phys. Rev. Lett. **67**, 228 (1991).

¹⁴S. Engelesberg and J. R. Schrieffer, Phys. Rev. **131**, 993 (1963).

¹⁵W. L. McMillan, Phys. Rev. **167**, 331 (1968).

¹⁶Q. Huang *et al.*, Nature **347**, 369 (1990).

¹⁷C. K. Loong *et al.*, Phys. Rev. Lett. **62**, 2628 (1989).