PHYSICAL REVIEW B **76**, 020501(R) (2007)

Muon spin relaxation and magnetic measurements on $Ba_{0.63}K_{0.37}BiO_3$: Evidence for polaronic strong-coupling phonon-mediated pairing

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(Received 15 May 2007; published 5 July 2007)

A penetration depth measurement was carried out on the optimally doped bismuthate superconductor $Ba_{0.63}K_{0.37}BiO_3$ (T_c=29.2 K) using the muon-spin-relaxation technique. We find that the temperature dependence of the penetration depth $\lambda(T)$ of this compound is in excellent agreement with strong-coupling phonon-mediated superconductivity with a reduced energy gap of $2\Delta(0)/k_BT_c$=4.4 and a retarded electron-phonon coupling constant $\lambda_{e\text{-}p}$=1.4. The observed large reduced energy gap rules out the possibility of pairing mechanisms based on coupling to high-energy electronic excitations. Quantitative data analyses indicate that high-temperature superconductivity in bismuthates arises from the Cooper pairing of polaronic charge carriers.

DOI: 10.1103/PhysRevB.76.020501 PACS number(s): 74.25.Ha, 74.20.Mn, 74.72.Hs

About 20 years after the discovery of high-temperature superconductivity in cuprate[1] and bismuthate[2,3] perovskite oxides, the microscopic pairing mechanism responsible for high-temperature superconductivity in these oxides remains elusive, despite tremendous experimental and theoretical efforts. Unlike the cuprate superconductors, which contain two-dimensional CuO_2 planes, the bismuthate $Ba_xK_{1-x}BiO_3$ has a cubic structure in its superconducting phase.[4] This suggests that two-dimensionality is not an essential condition for high-temperature superconductivity. The Bi-O network with itinerant Bi 6*s* conduction electrons excludes the possibility of any magnetic mechanism as suggested for the cuprate superconductors. Furthermore, bismuthate superconductors are characterized by a very low density of states at the Fermi level.[5] Such a low density of states requires a very large electron-phonon coupling strength to achieve this remarkably high transition temperature ($T_c\sim 30$ K) within the conventional phonon-mediated pairing mechanism. Too large an electron-phonon coupling strength will lead to a structural instability, which in turn destroys superconductivity. Therefore, an unconventional pairing mechanism is required to explain superconductivity in doped bismuthates. One possible unconventional mechanism is that the pairing is mainly mediated by a high-energy charge excitation.[6] This mechanism requires weak coupling, so that the reduced energy gap $2\Delta(0)/k_BT_c$ should be close to the value (3.53) predicted from the weak-coupling Bardeen-Cooper-Schrieffer theory. Another possible mechanism[7,8] is that strong coupling to high-energy phonon modes leads to the formation of polarons, and that the polarons are bound into Cooper pairs through a retarded electron-phonon interaction with low-energy phonon modes.

Here we report a penetration depth measurement on the optimally doped bismuthate superconductor $Ba_{0.63}K_{0.37}BiO_3$ (T_c=29.2 K) using the muon-spin-relaxation (μSR) technique. We find that the temperature dependence of the penetration depth $\lambda(T)$ of this compound is in excellent agreement with strong-coupling phonon-mediated superconductivity with a reduced energy gap of $2\Delta(0)/k_BT_c$=4.4 and a retarded electron-phonon coupling constant $\lambda_{e\text{-}p}$=1.4. The observed large reduced energy gap rules out the possibility of pairing mechanisms based on the coupling to high-energy electronic excitations. Quantitative data analyses indicate that high-temperature superconductivity in bismuthates arises from the Cooper pairing of polaronic charge carriers, whose masses are enhanced by a factor of about 2.8. We discuss the importance of the polaronic effect in the enhancement of superconductivity.

Samples of $Ba_{0.63}K_{0.37}BiO_3$ were prepared by conventional solid state reaction.[9] The field-cooled magnetization in fields from 5 Oe to 50 kOe was measured by a Quantum Design superconducting quantum interference device magnetometer. Transverse-field μSR (TFμSR) measurements were performed on beamline πM3 at the Paul Scherrer Institute (PSI), Switzerland, using low-momentum muons ($\sim$29 MeV/c).

The muon time spectra were analyzed with two Gaussian components.[10] Analysis of the time spectra below T_c showed that more than 70% of the muons stop in the superconducting regions (broad component). In these regions, the internal magnetic field is smaller than the external one because of the diamagnetic screening, and the depolarization rate is much higher than that in the normal state because of the formation of the vortex lattice. The remaining 30% of the muons (narrow component) oscillate with a frequency nearly equal to that corresponding to the applied magnetic field. This signal generally comes from the muons stopping in the sample plate and at nonsuperconducting grain boundaries, as often observed in polycrystalline superconductors.[11]

For polycrystalline superconductors, the envelope of the muon precession signal has approximately a Gaussian form $\exp(-\sigma^2t^2/2)$ and the depolarization rate $\sigma=\sqrt{\sigma_L^2+\sigma_N^2}$, where σ_L is the spin depolarization rate due to the perturbation of the vortex lattice, and $\sigma_N\simeq 0.1\ \mu s^{-1}$ is the spin depolarization rate due to nuclear dipole fields. It is shown that σ_L is proportional to the superfluid density $1/\lambda^2$ (Ref. 12). For nearly-isotropic-type superconductors, the magnetic penetration depth λ is given by[12,13]

$$\lambda = \frac{280\ (\text{nm})}{\sqrt{\sigma_L(\mu s^{-1})}}. \qquad (1)$$

Figure 1(a) shows the temperature dependence of σ for $Ba_{0.63}K_{0.37}BiO_3$. The horizontal line indicates the depolariza-

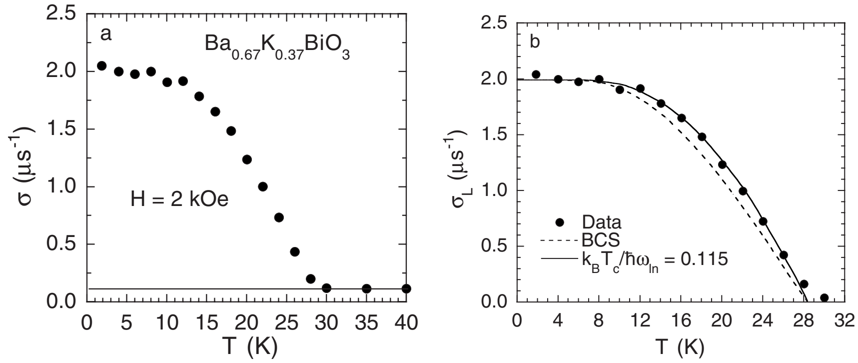

FIG. 1. (a) Temperature dependence of the depolarization rate σ for $Ba_{0.63}K_{0.37}BiO_3$. The horizontal line indicates the depolarization rate σ_N contributed from nuclear dipole fields. (b) Temperature dependence of σ_L. The error bars below 15 K are close to the symbol size, while the error bars above 15 K are shorter. The solid line is the expected curve for a phonon-mediated clean superconductor with $k_BT_c/\hbar\omega_{\ln}=0.115$ (see Fig. 111 of Ref. 15), a fixed $T_c=28.4$ K in the field of 2 kOe, as determined from magnetization measurements (see Fig. 3 below), and $\sigma_L(0)=1.991$ μs^{-1}. The slope of the curve near T_c corresponds to $d(\Phi_0/\lambda^2)/dT=-45.1$ Oe/K.

tion rate σ_N contributed from nuclear dipole fields. The value of σ_L is calculated using $\sigma_L=\sqrt{\sigma^2-\sigma_N^2}$. In Fig. 1(b), we show σ_L versus temperature. It is clear that the temperature dependence of σ_L is consistent with s-wave gap symmetry. The absence of linear temperature dependence at low temperatures also indicates that the contribution due to thermally activated flux depinning is negligible.[14] The solid line is the expected curve for a phonon-mediated clean superconductor with $k_BT_c/\hbar\omega_{\ln}=0.115$ (where $\hbar\omega_{\ln}$ is the logarithmic mean phonon energy), a fixed $T_c=28.4$ K in the field of 2 kOe, as determined from magnetization measurements (see Fig. 3 below), and $\sigma_L(0)=1.991$ μs^{-1}. The value of $\sigma_L(0)$ corresponds to $\lambda(0)=1985$ Å. From the slope of the curve near T_c, we find that $d(\Phi_0/\lambda^2)/dT=-45.1$ Oe/K.

We can determine the reduced energy gap from the value of $k_BT_c/\hbar\omega_{\ln}=0.115$ using a standard expression[15]

$$\frac{2\Delta(0)}{k_BT_c}=3.53\left[1+12.5\left(\frac{k_BT_c}{\hbar\omega_{\ln}}\right)^2\ln\left(\frac{\hbar\omega_{\ln}}{2k_BT_c}\right)\right]. \quad (2)$$

Substituting $k_BT_c/\hbar\omega_{\ln}=0.115$ into Eq. (2) yields $2\Delta(0)/k_BT_c=4.4$. The large reduced energy gap indicates that $Ba_{0.63}K_{0.37}BiO_3$ is a strong-coupling superconductor. The large reduced gap also excludes the possibility of pairing mechanisms based on high-energy electronic excitations. Thus, the present result clearly demonstrates a predominantly phonon-mediated pairing mechanism in the bismuthate superconductors.

We can also determine the Ginzburg-Landau parameter κ from the standard expressions[16] $2\kappa^2/\ln\kappa=(dH_{c2}/dT)/(dH_{c1}/dT)$ and $dH_{c1}/dT=(\ln\kappa/4\pi)[d(\Phi_0/\lambda^2)/dT]$ if we independently evaluate the slope dH_{c2}/dT of the upper critical field near T_c. For conventional superconductors, where superconducting fluctuation is negligible, the value of dH_{c2}/dT can be reliably determined from electrical and magnetic measurements. However, for high-temperature cuprate and bismuthate superconductors, superconducting fluctuation is significant, so that the critical fields determined from electrical and magnetic measurements are not true thermodynamic upper critical fields, as shown clearly by Cooper *et al.*[17] One example of this significant fluctuation effect is shown in Fig. 2, where we plot the phase diagram of $H_{c2}(T)$ and $H_R^*(T)$ for the electron-doped $Sm_{1.85}Ce_{0.15}CuO_{4-y}$. Here, $H_R^*(T)$ is determined from $R(T,H)$ data using the onset temperature in the transition curve, and the intrinsic thermodynamic upper critical field $H_{c2}(T)$ is determined from the superconducting fluctuation analysis of $R(T,H)$ data.[18] One can clearly see that the $H_{c2}(T)$ data agree very well with Werthamer-Helfand-Hohenberg theory with $H_{c2}(0)=97.2$ kOe (solid line). In contrast, $H_R^*(T)$ shows an upward curvature. It is remarkable that the $H_R^*(T)$ data can be well fitted by a second-order polynomial function with $H_R^*(0)=97.2$ kOe (dashed line). This implies that $H_{c2}(0)=H_R^*(0)$, as expected from the theory of thermodynamic fluctuations.[17] Therefore, only the zero-temperature upper critical field can be reliably determined from electric and magnetic measurements.

Figure 3(a) shows the field-cooled magnetizations of $Ba_{0.63}K_{0.37}BiO_3$ in fields of 5 Oe and 5 kOe, respectively. We define the critical temperature as the point of intersection

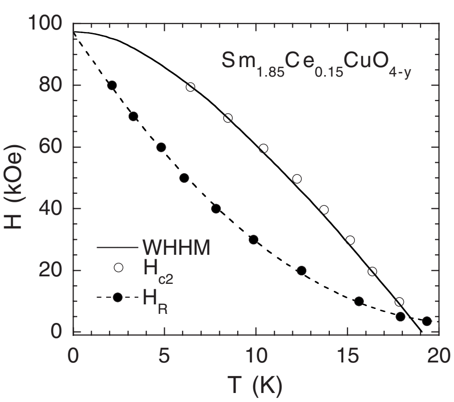

FIG. 2. Phase diagram of $H_R^*(T)$ and $H_{c2}(T)$ for $Sm_{1.85}Ce_{0.15}CuO_{4-y}$. Here $H_R^*(T)$ is determined from $R(T,H)$ data using the resistive onset temperature, and the intrinsic thermodynamic critical field $H_{c2}(T)$ is determined from the superconducting fluctuation analysis of $R(T,H)$ data (Ref. 18).

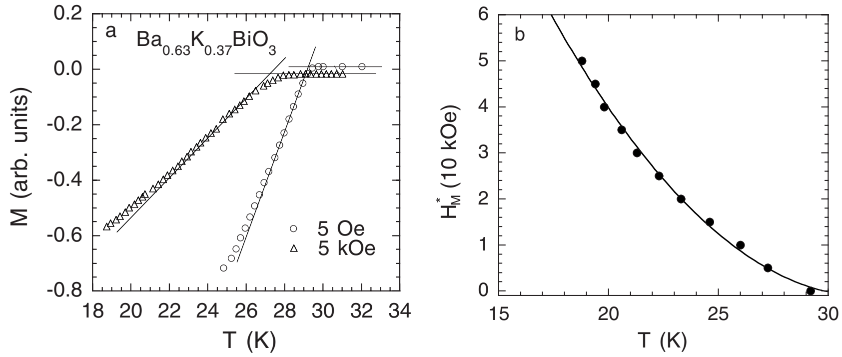

FIG. 3. (a) Field-cooled magnetization of $Ba_{0.63}K_{0.37}BiO_3$ in the fields of 5 Oe and 5 kOe, respectively. (b) Critical-field phase diagram of $Ba_{0.63}K_{0.37}BiO_3$. The solid line is the best-fitted curve by a second-order polynomial function $H^*_M(T)=297-18.8T+0.29T^2$ kOe.

between the extrapolated linear normal-state baseline and the extrapolated linear slope of the diamagnetic transition[19] [see the solid lines in Fig. 3(a)]. With this definition, we obtain the phase diagram of the magnetically determined critical field $H^*_M(T)$ for this bismuthate superconductor, as shown in Fig. 3(b). It is apparent that $H^*_M(T)$ shows an upward curvature, in agreement with the previous results.[19,20] The solid line is the best-fitted curve by a second-order polynomial function $H^*_M(T)=297-18.8T+0.29T^2$ kOe. It is interesting that this polynomial function obtained from the best fit to the present data in a limited temperature region agrees well with that obtained from the best fit to data down to 4.2 K (Ref. 20). Furthermore, it was shown[19–21] that the electrically determined critical field $H^*_R(T)$ nearly coincides with the magnetically determined $H^*_M(T)$. This suggests that the critical fields obtained from both magnetic and electrical measurements are associated with the same physical phenomenon. Using $H_{c2}(0)=H^*_M(0)$ (see Fig. 2 and Ref. 17), we obtain $H_{c2}(0)=297$ kOe for $Ba_{0.63}K_{0.37}BiO_3$, leading to a zero-temperature coherence length $\xi(0)=(\Phi_0/2\pi H_{c2})^{1/2}=33.3$ Å (where Φ_0 is the quantum of flux). The values of $H_{c2}(0)$ and $\xi(0)$ for our sample are nearly the same as those reported previously.[20,21]

Now we turn to quantitative data analyses based on a modified strong-coupling phonon-mediated mechanism,[7,8] where strong coupling to high-energy phonon modes leads to the formation of polarons, and the polarons are bound into Cooper pairs through a retarded electron-phonon interaction with low-energy phonon modes. Within this model, the polaronic effect simply narrows the bandwidth by a factor of f_p, so that the density of states and the retarded electron-phonon coupling constant $\lambda_{e\text{-}p}$ increase by the same factor. The total mass enhancement factor f_t within this model is then given by

$$f_t = f_p(1+\lambda_{e\text{-}p}). \tag{3}$$

The enhancement factor $1+\lambda_{e\text{-}p}$ arises from the retarded electron-phonon interaction, which is treated within the Migdal approximation.

Substituting $k_BT_c/\hbar\omega_{\ln}=0.115$ into several empirical formulas for conventional superconductors,[15] we determine $\lambda_{e\text{-}p}=1.4$, $h_{c2}=H_{c2}(0)/[T_c(dH_{c2}/dT)]=0.75$, and $\Delta C/\gamma T_c=2.5$. Here ΔC is the specific-heat jump at T_c, and γ is the electronic specific-heat coefficient. Since the bismuthate superconductor might not be in the clean limit, all the values of $k_BT_c/\hbar\omega_{\ln}$, $\lambda_{e\text{-}p}$, h_{c2}, and $\Delta C/\gamma T_c$ may be overestimated.[15] Using $h_{c2}=H_{c2}(0)/[T_c(dH_{c2}/dT)]=0.75$, $H_{c2}(0)=297$ kOe, and $T_c=29.2$ K, we obtain $dH_{c2}/dT=-13.58$ kOe/K. We then determine the Ginzburg-Landau parameter κ and dH_c/dT from the standard expressions[16]

$$2\kappa^2/\ln\kappa = (dH_{c2}/dT)/(dH_{c1}/dT),$$

$$dH_{c1}/dT = (\ln\kappa/4\pi)[d(\Phi_0/\lambda^2)/dT],$$

and $dH_c/dT=(dH_{c2}/dT)/(\kappa\sqrt{2})$. Substituting $dH_{c2}/dT=-13.58$ kOe/K and $d(\Phi_0/\lambda^2)/dT=-45.1$ Oe/K into the above expressions, we obtain $\kappa=43.4$ and $dH_c/dT=-221$ Oe/K. Then, using $\Delta C/T_c=(1/8\pi\kappa^2)(dH_{c2}/dT)^2$ (Ref. 19) and $\Delta C/\gamma T_c=2.5$, we find $\gamma=7.41$ mJ/mol K^2. The band density of states at the Fermi level is calculated to be 0.46 states/eV per cell for $x=0.4$,[5] corresponding to a band electronic specific-heat coefficient $\gamma_b=1.1$ mJ/mol K^2. The total mass enhancement factor $f_t=\gamma/\gamma_b=6.74$. From Eq. (3) and with $\lambda_{e\text{-}p}=1.4$, we then find that $f_p=2.8$. This polaron enhancement factor should be underestimated since we may overestimate $k_BT_c/\hbar\omega_{\ln}$ due to the finite mean free path. Optical experiments show that the Drude weight just above T_c is reduced by a factor of about 12 compared with the total optical weight for free carriers.[22] This result may suggest that $f_t\leq 12$, in agreement with $f_t\geq 6.74$ deduced above.

Our data analyses are justified only if the upward curvature of $H^*_M(T)$ or $H^*_R(T)$ is indeed caused by thermodynamic fluctuations. Applying the model of thermodynamic fluctuations to the $H^*_R(T)$ data of a $Ba_{1-x}K_xBiO_3$ crystal, Cooper *et al.* obtain a fitting parameter $T_0(0)=60$ K, where

$$T_0(0) = \frac{H_c^2(0)\xi^3(0)}{8k_B\pi\beta}, \tag{4}$$

and β is a numerical factor of order unity.[17] Using $dH_c/dT=-221$ Oe/K, $T_c=29.2$ K, and the relation $H_c(T)=H_c(0)[1-(T/T_c)^2]$, we find $H_c(0)=3228$ Oe. Substituting $\beta=1$, $H_c(0)=3228$ Oe, and $\xi(0)=33$ Å into Eq. (4) yields $T_0(0)=108$ K, in quantitative agreement with the fitting parameter (60 K). This quantitative agreement clearly indicates that the upward curvature of the critical fields is indeed caused by superconducting fluctuations, which justifies our data analyses.

It is interesting that the polaron mass enhancement factor f_p in $BaPb_{0.79}Bi_{0.21}O_3$ can be estimated from the density of states inferred from the ^{17}O Knight shift. The average ^{17}O Knight shift at low temperatures is about 375 ppm for $BaPb_{0.79}Bi_{0.21}O_3$, which corresponds to a "bare" density of states $N(0)=0.40$ states/eV per cell.[23] The bare density of states deduced from the Knight shift is enhanced by a factor of 2 compared with the band density of states (0.20 states/eV per cell).[24] This enhancement factor cannot arise from the Stoner effect, which should be negligible for s conduction electrons. On the other hand, this enhancement factor can arise from the polaronic effect,[7] that is, $f_p=2$. Therefore, the f_p values of the two optimally doped bismuthate superconductors are quite similar.

Since $\lambda_{e\text{-}p} \propto f_p$, the value of f_p implies that $\lambda_{e\text{-}p}$ is enhanced by a factor of about 2.8 due to the polaronic effect. Without the polaronic effect, $\lambda_{e\text{-}p}$ would be about 0.5 for $Ba_{0.63}K_{0.37}BiO_3$. Substituting $\lambda_{e\text{-}p}=0.5$, the Coulombic pseudopotential $\mu^*=0.1$, and $\hbar\omega_{\ln}=21.3$ meV into the McMillan formula[15]

$$k_B T_c = \frac{\hbar\omega_{\ln}}{1.2} \exp\left(-\frac{1.04(1+\lambda_{e\text{-}p})}{\lambda_{e\text{-}p} - \mu^*(1+0.62\lambda_{e\text{-}p})}\right), \quad (5)$$

we find that $T_c=3.0$ K. Therefore, the highest T_c in bismuthates would be about 3 K if there were no polaronic effect. This suggests that the polaronic effect should play an important role in achieving high-temperature superconductivity.

Now we discuss the isotope effects within this pairing mechanism. It is known that, when the characteristic energy $\hbar\omega_0$ of phonon modes involved in the polaron formation is larger than the bare hopping integral t, the polaron mass enhancement factor is given by[25] $f_p=\exp(A/\omega_0)$, where A is a constant. The total exponent of the isotope effect on f_p is $\alpha_f=\Sigma - d\ln f_p/d\ln M_j = -0.5\ln f_p$, where M_j is the mass of the jth atom. On the other hand, for $t>\hbar\omega_0$, as in bismuthates, one expects that $-\alpha_f < 0.5\ln f_p$. Because $\lambda_{e\text{-}p} \propto f_p$ within this pairing mechanism, the total exponent α_λ of the isotope effect on $\lambda_{e\text{-}p}$ is the same as α_f, that is, $-\alpha_\lambda < 0.5\ln f_p$. With $f_p=2.8$, one has $-\alpha_\lambda < 0.51$. The finite positive value of $-\alpha_\lambda$ reduces the isotope effect on T_c, in agreement with the experiments.[6,9]

In summary, the penetration depth of the bismuthate superconductor $Ba_{0.63}K_{0.37}BiO_3$ was measured by the muon-spin-relaxation technique. The temperature dependence of the penetration depth $\lambda(T)$ of this compound indicates a large reduced energy gap of $2\Delta(0)/k_B T_c=4.4$. The observed large reduced energy gap rules out the possibility of pairing mechanisms based on coupling to high-energy electronic excitations. Quantitative data analyses suggest that high-temperature superconductivity in bismuthates arises from the Cooper pairing of polaronic charge carriers.

This work was partly performed at the Swiss Muon Source (SμS), Paul Scherrer Institute (PSI, Switzerland). The author is grateful to R. Khasanov, A. Shengelaya, D. Herlach, and A. Amato for assistance in μSR measurement and analysis.

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