Density of States and Isotope Effect in BiO Superconductors: Evidence for Nonphonon Mechanism

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We report measurements of the physical properties of the 30-K superconductor $Ba_{0.6}K_{0.4}BiO_3$, including upper and lower critical fields and normal-state susceptibility. From the results and from comparison with $BaPb_{0.75}Bi_{0.25}O_3$ and band-structure calculations it is concluded that the BiO superconductors are in the weak-coupling limit, implying that the anomalously high T_c's are not due to conventional, strong electron-phonon coupling. A sizable oxygen isotope effect of very similar magnitude is found for both compounds ($\alpha = 0.2$–0.25). We speculate that "phononic" effects in these materials are actually only indicative of dressed electronic excitations mediating superconducting pairing.

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When superconductivity in $BaPb_{0.75}Bi_{0.25}O_3$ (BPBO) was discovered in 1975, the T_c of ~ 12 K was considered remarkable for a nontransition-metal compound.[1] The exceptional status of this compound was recognized only later, however, when detailed studies on single crystals revealed a very small electronic density of states $N^*(0)$ at the Fermi level.[2–5] The T_c of 12 K is about 3–5 times higher than in all other superconductors with comparable $N^*(0)$, including other oxides. The presence of a very strong interaction of electrons with high-frequency phonons was widely invoked to account for the high T_c, but without quantitative success. Moreover, lattice-dynamics studies could not detect the band of "breathing" type vibrations which were expected to couple strongly to the electrons.[6]

A particularly puzzling and apparently self-contradictory experimental result was found in electron tunneling spectroscopy: The quasiparticle density of states is as strongly modified by electron-phonon interaction as it is in Pb,[2] but it is only strong enough to give a T_c of a few degrees.[7] In contrast, the gap value $2\Delta/k_BT_c = 3.5 \pm 0.1$ is indicative of weak coupling. In light of the discovery of Cu-O based superconductors[8] (with T_c's now approaching 150 K) and the fact that their $T_c/N^*(0)$ ratio is also unusually large, our interest has returned to the prototypical high-T_c superconductors based on BiO, mainly to study the possibility of a common novel pairing mechanism.

The question about the pairing mechanism in high-T_c superconductors can now be addressed in a new way since the discovery of superconductivity at 30 K in $Ba_{0.6}K_{0.4}BiO_3$ (BKBO).[9,10] Both BPBO and BKBO are simple perovskites. Their electronic structures are essentially the same, with a single band crossing the Fermi level.[11] The two Bi-O based superconductors can thus be seen as the "same compound" except that the Fermi level in BKBO is higher than in BPBO.

Here we report measurements of some of the basic physical properties of the 30-K T_c superconductor $Ba_{0.6}K_{0.4}BiO_3$, including critical fields, normal-state susceptibility, and oxygen isotope effect. We establish that BKBO is indeed a high-T_c superconductor [with a large $T_c/N^*(0)$ ratio] and that it is "nonmagnetic" in that $\chi(T)$ in the normal state is diamagnetic, weakly temperature dependent, and dominated by a large core diamagnetism with a small paramagnetic contribution ($\sim 1.10^{-5}$ emu/mol). From the slopes of the thermodynamic critical fields of BKBO and BPBO, and also from comparison with band-structure calculations, we conclude that the BiO superconductors are in the weak-coupling limit. We find further that the oxygen isotope effect is the same for both BPBO and BKBO, with an α_0 of ~ 0.2–0.25. These results suggest a "nonmagnetic" pairing mechanism, and we speculate that it could be coupling through electronic excitations with a "parasitic" lattice deformation, but not conventional phonon-mediated pairing.

Samples of BKBO were prepared as described in detail elsewhere.[10] These materials are high-quality single-phase cubic perovskites with good homogeneity as evidenced in their narrow x-ray diffraction line profiles at high diffraction angles.[12] The synthesis, which involves the reaction of KO_2, BaO, and Bi_2O_3 in crimped silver tubes placed inside evacuated quartz tubes, is somewhat difficult and relies in part on a slow leaking of the silver during the course of the reaction. We find, however, that this technique results in more highly uniform materials with larger volume fractions of superconductivity than those prepared by a simpler method.[13] Starting material for the isotope exchange was fully oxidized in flowing ^{16}O at 475 °C for 1 h before the exchange reactions. Isotope exchange in $BaPb_{0.75}Bi_{0.25}O_3$ was performed in pulverized single crystals grown by a flux technique.[4]

The normal-state susceptibility $\chi(T)$ was calculated from high-field magnetization curves (Fig. 1). Over the entire temperature range χ is negative and some scatter is found among the various samples (similar values are reported also in Ref. 14). Our earliest data, as we had suspected, were dominated by extraneous paramagnetic contributions.[10] The core diamagnetism is estimated

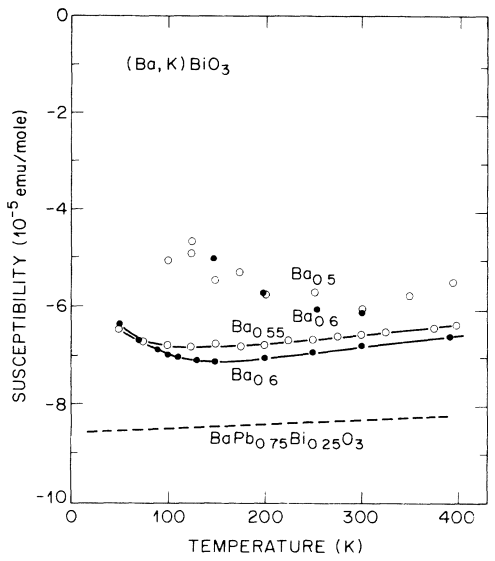

FIG. 1. Normal-state susceptibility of $(Ba,K)BiO_3$ and $BaPb_{0.75}Bi_{0.25}O_3$. The diamagnetic core contribution is 7.8 $\times 10^{-5}$ emu/mol for the former and 8.6×10^{-5} emu/mol for the latter.

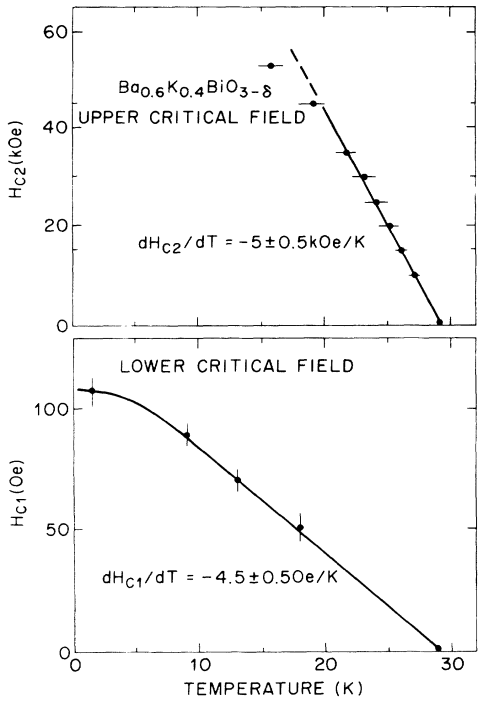

FIG. 2. Upper and lower critical fields of $Ba_{0.6}K_{0.4}BiO_3$, from which the slope of the thermodynamic critical field is calculated as 75 ± 8 Oe/K.

from published values and our own measurements on reference compounds ($\chi_c \cong -7.8\times10^{-5}$ emu/mol). The paramagnetic contribution from the valence electrons is small and lies between ~ 0.8 and $\sim 2\times10^{-5}$ emu/mol. The positive slope $d\chi/dT$ ($\sim 2\times10^{-8}$ emu/mol K) is larger by about a factor of 2 than in single crystals of BPBO. Details will be discussed elsewhere (see also Ref. 15 for BPBO). Thus, the BiO superconductors are not "magnetic" in the sense that no indication of either intrinsic local moment behavior or enhanced band susceptibility is found. This is hardly surprising as bismuth is not known to support magnetism due to the instability of the s^1 configuration.

Measurements of the upper and lower critical fields, H_{c1} and H_{c2}, are particularly useful in these compounds because they are intensive quantities and the extraction of superconducting parameters does not depend on the superconducting volume fraction. H_{c1} is determined from $M(H)$ curves where $M(H)$ deviates from linearity. The results for BKBO are shown in the lower panel of Fig. 2. The upper critical field was also measured magnetically in $M(T)$ scans in constant fields. The temperature at which $M(T)$ starts deviating from the normal-state value is taken as $T_c(H)$ and this allows for a reproducible and well-defined determination of $H_{c2}(T)$, shown in the upper panel of Fig. 2. Even for T_c's which differ by 1–2 K in various samples, the H_{c2} slope, H'_{c2}, remains the same within 5%. We note the linear T dependence of H_{c2} near T_c for both BPBO and BKBO.

Samples for oxygen-isotope-effect studies were prepared with the well controlled gas-phase exchange method introduced in Ref. 16. Two pieces of the same starting material are treated identically, except that one is exposed to ^{18}O and the other to ^{16}O. The containers holding the two samples are placed side by side in a furnace which guarantees that sample and reference experience identical thermal cycling. Oxygen was exchanged in BKBO in three steps: 6 h at 340 °C, an additional 12 h at 340 °C, and finally 24 h more at 350 °C. The change of T_c after the first step was 0.05 ± 0.03 K, after the second step 0.24 ± 0.03 K, and after the third step 0.45 ± 0.03 K. T_c of the ^{16}O reference remained unchanged. In Fig. 3, the results after step three are shown as $M(T)$, normalized to the sample weight. Rounding of the transition is expected as a result of the fine-grained nature of the samples and a measuring field of 25 Oe, which is not small compared to H_{c1}. Thus, 30% flux exclusion for $T \rightarrow 0$ underestimates the superconducting volume considerably. Full diamagnetism ($> 90\%$) is observed in $M(H)$ measurements for H_{c1}, indicating high sample quality. The isotope ratio was determined by mass spectroscopy of the evolving gas as the samples were heated to 1250 °C at a rate of 5 °C/s. All oxygens occupy equivalent lattice sites, eliminating any potential concern about exchange of only a subset of oxygen atoms. After the third step, $65\% \pm 4\%$ of oxygen is present as ^{18}O. BPBO was isotope exchanged at 750 °C for three days, resulting in samples with $85\% \pm 5\%$ ^{18}O. The shifts in T_c for BKBO and BPBO are shown in Figs. 3 and 4. A quantitative measure of the isotope effect is

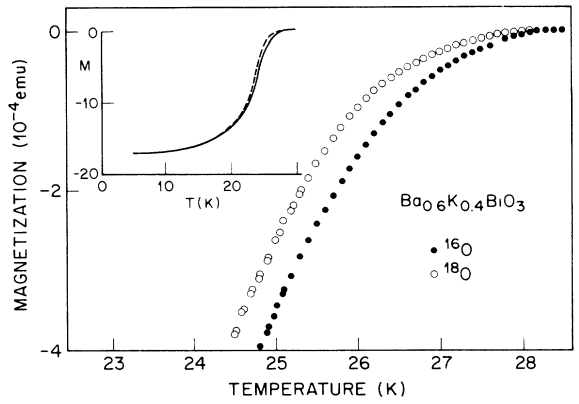

FIG. 3. Shift of the T_c due to exchange of ^{18}O for ^{16}O in $Ba_{0.6}K_{0.4}BiO_3$. 65% ± 4% of oxygen is present as ^{18}O, resulting in an isotope effect exponent of 0.21 ± 0.03.

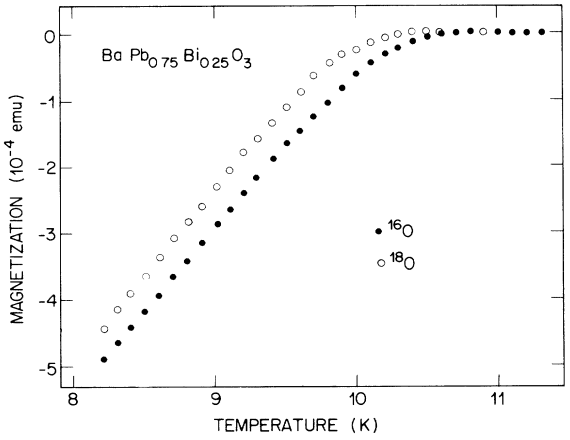

FIG. 4. Isotope effect in $BaPb_{0.75}Bi_{0.25}O_3$. (85% ± 5% ^{18}O, $\alpha = 0.22 \pm 0.03$.)

given by the exponent α, defined as $T_c \sim M^{-\alpha}$. For BKBO, we calculate $\alpha = 0.21 \pm 0.03$, and for BPBO we calculate $\alpha = 0.22 \pm 0.03$, with T_c's of 28 and 10.5 K, respectively. (The value of $\alpha \sim 0.6$–0.75 for BPBO reported in Ref. 17 appears suspect.) The result will be discussed later in the context of the other conclusions.

In the following, we analyze the critical fields to extract the density of states, and we make comparisons with BPBO and band-structure calculations. The slopes of H_{c1} and H_{c2} are 4.5 ± 0.5 and 5000 ± 500 Oe/K, respectively. Using standard expressions, we calculate the slope of the thermodynamic critical field H_c to be 75 ± 8 Oe/K and $\kappa_{GL} \cong 45$. In BPBO, H_c' is 50 ± 5 Oe/K, and $\kappa \simeq 80$.[4,5] The large κ values are partly due to the small carrier concentration (2.5×10^{21} cm^{-3} for BPBO; 4–5×10^{21} cm^{-3} estimated for BPBO) and a resulting large penetration length. (The Ginzburg-Landau coherence length in BPBO is significantly larger[4,5] than in the cuprate superconductors: 60–80 Å vs ~20 Å.) If we assume a second-order phase transition at T_c, the specific-heat anomaly ΔC can be calculated from H_c'. For $\Delta C/T_c = (H_c')^2 V_{mol}/4\pi$ we get 2.1 ± 0.4 mJ/mol K^2 with $V_{mol} = 47.6$ cm^3. The same quantity is ~0.94 mJ/mol K^2 in BPBO, smaller by a factor of ~2.2 ± 0.4. This ratio of 2.2 can be compared with band-structure calculations. Using the same linearized augmented-plane-wave scheme for Ba(Pb,Bi)O_3 and for (Ba,K)BiO_3 with a choice of the band filling appropriate for the actual chemical composition, the bare density of states $N(0)$ are 0.24 states/eV for $BaPb_{0.75}Bi_{0.25}O_3$ and 0.46 states/eV for $Ba_{0.6}K_{0.4}BiO_3$ (Ref. 10). $\Delta C/T_c$ is proportional to the dressed density of states $N^*(0) = N(0) \times (1+\lambda)$, with λ being the coupling parameter. The observation that the ratios of $N^*_{BKBO}(0)/N^*_{BPBO}(0)$ and $N_{BKBO}(0)/N_{BPBO}(0)$ are essentially the same severely restricts the values of λ.

We note that comparing ratios of $\Delta C/T_c$ eliminates in the first approximation the uncertainties due to strong-coupling effects in converting $\Delta C/T_c$ into $N^*(0)$. (Besides, the difference between 2.2 ± 0.4 and 1.9 allows for enough room to absorb small numerical corrections.) Most important, however, is the fact that the ratios can only be so close for either weak coupling ($\lambda \lesssim 1$) or for very strong coupling ($\lambda \gg 1$). The second possibility can be ruled out readily by extraction of numerical values of $N^*(0)$ from $\Delta C/T_c$. Using the BCS relationship, which gives upper limits for $N^*(0)$, we find that the values of $N^*(0)$ are quite comparable to the calculated $N(0)$'s: 0.15 ± 0.3 vs 0.24 for BPBO, and 0.32 ± 0.07 vs 0.46 for BKBO. [Earlier estimates from different measured quantities gave $N^*(0)$ of 0.25–0.32 for BPBO; Refs. 4 and 5.] For the sake of the present argument, we conclude that $N(0)$ and $N^*(0) = N(0)(1+\lambda)$ are the same within ±40%. [Considering various sources of uncertainties, we would estimate that λ does not exceed 0.6–0.8. To obtain T_c's of ~30 K even with large characteristic Debye temperatures of 150–200 K, λ would have to be of the order 1.5–2, and $N^*(0)$ would be much larger than measured.] Thus, the BiO high-T_c superconductors are in the weak-coupling regime, implying that their anomalously high T_c is not due to conventional, strong electron-phonon coupling.

The sizable oxygen isotope effect ($\alpha = 0.2$–0.25), which is very similar for both compounds, adds to the problem of explaining the high T_c's within the conventional framework. We refrain from searching for a "consistent" set of parameters $\langle\omega\rangle$, λ, and μ^*, even if they existed formally, since we doubt that the numerical expressions are applicable to these compounds.

The various experimental data lead us to suggest that pairing is mediated by electronic excitations which involve atomic displacements as a result of charge redistribution.[18] Such a scenario with a high-energy excitation (0.1–0.5 eV), would account for high T_c's despite weak coupling, and for the observation of "phononic effects." We consider the isotope effect and the modified tunnel-

ing spectra as expressions of such "parasitic" phonon involvement.[19] The value of the superconducting gap $2\Delta = 3.5kT_c$ and the absence of significant density-of-states enhancement are the key signatures of weak coupling. When λ is expressed in terms of the coupling function $\alpha^2F(\omega)$, the low-energy phonon part and the high-energy electronic part would scale in the same way as the total coupling λ does. The scaling is mainly given by the density of states $N(0)$. The main contribution to λ would come from the electronic part, and the isotope effect α would remain the same.

In summary, we have measured several basic physical parameters of the 30-K superconductor $Ba_{0.6}K_{0.4}BiO_3$ and compared them with $BaPb_{0.75}Bi_{0.25}O_3$. From the analysis of the density of states, we conclude that these two high-T_c BiO superconductors are in the weak-coupling limit. We find the same oxygen isotope effect in both compounds and suggest that electron pairing be mediated by electronic excitations which would account for the new as well as earlier results.

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[19]After finishing this work, we received a preprint by M. Tachiki and S. Takahashi [Phys. Rev. B **38**, 218 (1988)] where the isotope effect is calculated for a model of pairing mediated by a combination of charge fluctuations and LO phonons. The conclusions are consistent with experimental results.