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Superconductivity above 20 K in the Ba-K-Bi-O system

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The results of magnetic susceptibility measurements on multiphase Ba-K-Bi-O samples with overall composition $Ba_{0.9}K_xBiO_3$ ($x \approx 0.2$) provide evidence for superconductivity above 20 K in a minority fraction ($\sim 5\%$) of the sample volume. These results support the expectation that K doping at the inactive Ba donor sites can extend the metallic range of the previously studied $BaPb_{1-x}Bi_xO_3$ alloys closer to the $BaBiO_3$ Peierls instability where the strong coupling of the conduction electrons to the O phonons could explain the enhanced ($T_c \sim 22$ vs 13 K) superconducting transition temperatures.

The $BaPb_{1-x}Bi_xO_3$ alloys[1] are notable ancestors to the rapidly growing family of perovskite-type high-temperature superconducting oxides that presently includes the La-Ba-Cu-O ($T_c \sim 30$ K) (Ref. 2) and Y-Ba-Cu-O ($T_c \sim 90$ K) (Ref. 3) systems as well as many chemically related compounds. According to the initial studies by Sleight, Gillson, and Bierstedt,[1] these $BaPb_{1-x}Bi_xO_3$ alloys exhibit superconductivity in the Pb-rich composition range $0.05 \leq x \leq 0.3$, with a maximum $T_c \approx 13$ K near $x \approx 0.25$. A metal-semiconductor transition is observed at $x \approx 0.35$, with the semiconducting behavior continuing to the end-member compound $BaBiO_3$.

Electronic-structure calculations[4] for the $BaPb_{1-x}Bi_xO_3$ alloys predict a single broad conduction band that originates from strong σ-antibonding combinations of Pb-Bi ($6s$) and O ($2p$) states. This band is gradually filled in a rigid-band manner with increasing x until it is half-filled in $BaBiO_3$. Here, the combination of nearly perfect Fermi-surface nesting and strong coupling of the electronic states at E_F to O bond-stretching displacements[4] leads to a commensurate charge-density-wave (CDW) distortion in which the O octahedra that surround neighboring Bi sites are alternately expanded or compressed.[5] This breathing-type displacement of O octahedra opens a semiconductor gap over the Fermi surface which accounts for the semiconducting properties of $BaBiO_3$.

The mechanism by which this semiconducting behavior is extended over the intermediate composition range $0.35 \leq x < 1$ is less well understood. A recent proposal by Weber[6] attributes these semiconducting properties to a combination of static "breathing-type" incommensurate CDW's and chemical "ordering waves" on the Pb-Bi sublattice. The latter component exploits the ~ 3-eV orbital-energy difference for the Pb-Bi $6s$ states that form the conduction band. By means of model supercell calculations, Weber has shown that a combination of CDW's and ordering waves with the same x-dependent wave vector $\mathbf{Q}(x) = 2\mathbf{k}_F(x)$ can produce gaps over the Fermi surface within the composition range where semiconducting properties are observed. Both components are essential since these gaps disappear when either contribution is omitted.

These results suggest that it should be possible to suppress the ordering waves and extend the metallic regime in $BaPb_{1-x}Bi_xO_3$ closer to the half-filled band condition ($BaBiO_3$), where the electron-phonon interaction is a maximum,[7] by leaving the conducting Bi-O complex intact and instead doping substitutionally at the inactive Ba donor sites. This situation, which is analogous to that in $La_{2-x}(Ba,Sr)_xCuO_4$ (Refs. 8 and 9), is expected to produce marginal stability and enhanced T_c's. In earlier studies,[1,10] a combination of K and Pb doping in a $Ba_{0.9}K_{0.1}Pb_{0.75}Bi_{0.25}O_3$ sample has produced similar critical temperatures ($T_c \sim 12$ K) but sharper transitions than those observed in Pb-doped $BaPb_{0.75}Bi_{0.25}O_3$ samples.

In the present investigation we have carried out dc magnetization measurements on K-doped $Ba_{0.9}K_xBiO_3$ samples with $x \approx 0.2$. The results show that a minority fraction ($\sim 5\%$) of K-rich samples ($Ba_{0.9}K_{0.2}BiO_3$) exhibit a Meissner effect, indicating a superconducting transition temperature $T_c \approx 22$ K. Problems in attaching reliable electrical contacts to the samples have prevented resistivity measurements thus far.

Samples of $Ba_{1-x}K_xBiO_3$ and $Ba_{1-x}Rb_xBiO_3$ were prepared by mixing appropriate amounts of the raw materials $BaCO_3$, K_2CO_3, Rb_2CO_3, and Bi_2O_3. These were ground for 30 min under acetone in an agate mortar. These mixtures were heat treated at 900 °C for 2 h in Pt crucibles. This resulted in a partially melted mass; however, further experiments using material treated at 800 °C where there was no melting did not produce any evidence of superconductivity after subsequent processing. The partially melted material was again ground to a fine powder for 30 min in an agate mortar. This powder was pressed into disks about 1 mm thick and 11 mm in diameter. These were sintered at 900 °C for 2 h in flowing oxygen. Samples for magnetic measurements were cut from these sintered disks.

$Ba_{1-x}K_xBiO_{3-\delta}$ samples with composition $x = 0.20$ and 0.24 showed no evidence of superconductivity. However, when excess K (or Rb) was incorporated in the batch, then diamagnetism was observed for the following compositions: $Ba_{0.9}K_xBiO_{3-\delta}$ ($x = 0.20$ and 0.24) and $Ba_{0.9}Rb_{0.2}BiO_{3-\delta}$.

X-ray diffraction data showed the major phase (~ 92 vol%) to have a perovskite-type structure similar to $BaPb_{0.75}Bi_{0.25}O_3$. In some cases, the perovskite peaks

were slightly split, exhibiting shoulders on their high-angle sides. In all cases, there were minor impurity phases ($\sim$3% Bi_2O_3, $\sim$5% unidentified) present. The extent of possible deviations δ from full O stoichiometry have not been investigated.

Magnetization studies have been carried out on bar-shaped samples using a vibrating-sample magnetometer (VSM). The samples were oriented so that the applied magnetic field H was parallel to the long axis of the bar. The experimental procedure involved first cooling the sample to 5 K in zero field (<0.1 Oe) and then increasing the field to about 10 Oe. The observed diamagnetic signal is then a measure of the amount of flux excluded. The disappearance of this diamagnetic signal with increasing temperature yields T_c, the superconducting critical temperature at which the material goes normal. Similarly, cooling from above T_c with an applied field of typically 10 Oe measures the amount of flux expelled (Meissner effect). The onset temperature of the Meissner effect is again, of course, a measure of T_c.

It is generally accepted that the Meissner effect cannot be determined accurately from ac susceptibility measurements. In addition, it is occasionally suggested that VSM measurements do not determine correctly the magnitude of the Meissner effect. Straightforward, though somewhat tedious, calculations show[11] that this is not the case if the measurements are made in a uniform magnetic field, such as that obtained from a large (12-in. Varian with 6-in. tapered pole faces and a 2-in. gap) electromagnet of the type employed here.

Typical results are shown in Fig. 1, where we plot the normalized susceptibility χ_n as a function of the temperature for the sample with nominal composition $Ba_{0.9}K_{0.24}BiO_3$. The normalized susceptibility is $\chi_n = -f/4\pi(1-d)$, where d is the shape-dependent demagnetizing factor for the sample. For example, $d=0$ for an infinitely long cylinder with H parallel to the long axis and $d=\frac{1}{3}$ for a sphere. The fraction of the sample that is actually diamagnetic is denoted by f. According to the results shown in Fig. 1, 5.3% of the total flux is excluded when the sample is cooled in zero field. Similarly, after cooling from above T_c with $H=10$ Oe, 4.3% of the flux is expelled at about 6 K.

The data shown in Fig. 1 are for a $Ba_{0.9}K_{0.24}BiO_3$ rod with dimensions $0.99\times0.26\times0.14$ cm. Approximating this rod by a cylinder with a diameter equal to the average of the two short dimensions, we obtain $d=0.03$ (Ref. 12).

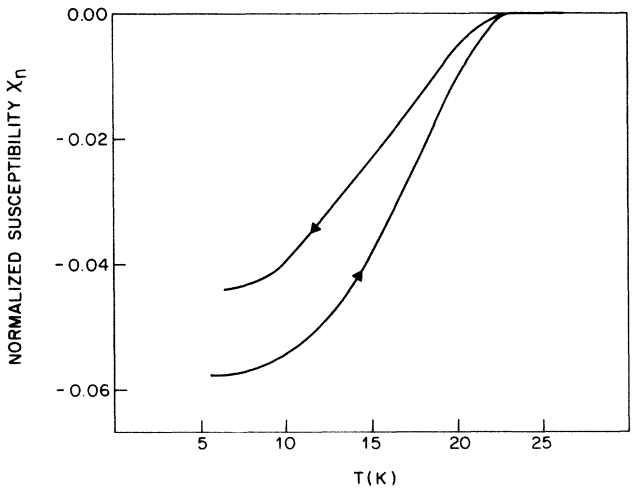

FIG. 1. Plot of the normalized susceptibility $\chi_n = -f/4\pi(1-d)$ as a function of temperature for $Ba_{0.9}K_{0.24}BiO_3$. The upper curve is obtained by cooling with an applied magnetic field $H=10$ Oe. The lower curve is obtained by cooling to 5 K in zero field, applying a magnetic field of 10 Oe, and then warming.

This value of d was used to determine χ_n. It is obvious that demagnetizing effects produce a small correction to the limiting case of an infinitely long cylinder for the present sample.

Similar results have been obtained for the K-doped sample with $x=0.20$ where $\sim$10% of the sample exhibited perfect diamagnetism. The $Ba_{0.9}Rb_{0.2}BiO_3$ sample exhibited a $T_c \approx 15$ K, though the diamagnetism ($\sim$5%) was significantly reduced.

To summarize, the present dc magnetization measurements provide evidence for superconductivity above 20 K in a polyphase material with overall composition $Ba_{0.9}K_xBiO_3$ and $x \approx 0.2$. Only a small fraction ($\sim$4%) of the sample exhibits the Meissner effect. Both the heating and cooling curves yield $T_c \approx 22$ K, which is notably higher than that obtained previously in $BaPb_{1-x}Bi_xO_3$ where $T_c \approx 13$ K for $x \approx 0.25$. In view of the fact that superconductivity has been observed only in small fractions of the sample volume, additional studies will be required in order to determine whether superconductivity is associated with the major perovskite-type phase or one of the minor impurity phases present.

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