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# Superconducting properties of the $Ba_{1-x}Rb_xBiO_3$ system

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Magnetization measurements revealed that $Ba_{1-x}Rb_xBiO_3$ exhibits superconductivity at $T_c = 29$ K in the $0.28 \leq x \leq 0.44$ range. In this range the room-temperature crystal structure belongs to the cubic phase. The $T_c$ value is independent of Rb concentration, although the lattice parameter decreases linearly with increasing $x$. Material parameters for $Ba_{0.6}Rb_{0.4}BiO_3$ are derived from measurements on the lower and upper critical fields. Comparison with $Ba_{0.6}K_{0.4}BiO_3$ shows that physical properties of the two superconductors are practically described by the same material parameters. The Sommerfeld parameter $\gamma$ is found to be 2.4 $\mathrm{mJ\,mole^{-1}K^{-2}}$, which is in good agreement with the value estimated from the normal-state susceptibility.

Since the discovery of the 30-K superconductor $Ba_{1-x}K_xBiO_3$,[1,2] several experimental studies have been carried out in order to investigate the physical properties in this system. One of the most prominent features in the $Ba_{1-x}K_xBiO_3$ system is the absence of magnetic order. Muon-spin-rotation[3] and magnetic-susceptibility[4,5] measurements support the interpretation[6,7] that the Bi(6$s$)-O(2$p$) bands in both $BaBiO_3$ and $Ba_{1-x}K_xBiO_3$ have nonmagnetic character. The situation in $Ba_{1-x}K_xBiO_3$ is in sharp contrast to the competition between antiferromagnetism and superconductivity in Cu-O-based compounds, such as $La_{2-x}Sr_xCuO_4$ (Ref. 8) and $YBa_2Cu_3O_{7-x}$.[9] The observations on oxygen-isotope effect in $Ba_{0.6}K_{0.4}BiO_3$ (Refs. 4 and 10) suggest that the electron-phonon interaction plays an important role in the superconducting pairing mechanism. According to the neutron[11,12] and x-ray diffraction[2,13,14] results, $Ba_{1-x}K_xBiO_3$ for $0.25 < x < 0.45$ exhibits a cubic perovskite structure both in superconducting and normal states. Based on critical-field measurements,[4,15] $Ba_{1-x}K_xBiO_3$ is regarded as an extreme type-II superconductor. This is similar in character to the 12-K superconductor $BaPb_{0.75}Bi_{0.25}O_3$.[16-18] In spite of the simultaneous discovery of superconductivity in $Ba_{1-x}K_xBiO_3$ and $Ba_{1-x}Rb_xBiO_3$,[1,2] we lack definite information concerning the superconducting properties of the Rb-substituted material. In this Rapid Communication, we present the superconducting range and the lattice parameter in $Ba_{1-x}Rb_xBiO_3$ as a function of $x$. Furthermore, we determine both lower and upper critical fields, and normal-state susceptibility. Then we derive material parameters describing superconducting properties. We compare the present results with those for $Ba_{0.6}K_{0.4}BiO_3$ and $BaPb_{0.75}Bi_{0.25}O_3$.

The powder samples used in this study were prepared using the two-step procedure invented for $Ba_{1-x}K_xBiO_3$ by Hinks *et al.*[11] Appropriate mixtures of $BaCO_3$, $Rb_2CO_3$, and $Bi_2O_3$ were calcined at 750 °C for 12 h in flowing $N_2$ gas, pulverized, and then annealed in $O_2$ at 400 °C for 1 h. We estimated the average grain size in the sample to be 5.5 $\mu$m using a HORIBA centrifugal particle analyzer.

The $Ba_{1-x}Rb_xBiO_3$ samples were characterized by powder x-ray diffraction at room temperature. For $0.28 \leq x \leq 0.44$, all the observed Bragg peaks were indexed on a cubic unit cell. By the analogy of the K-substituted crystal,[13] $Ba_{1-x}Rb_xBiO_3$ in the $0.28 < x < 0.44$ range is expected to have a cubic perovskite structure with space group $Pm3m$. As shown in Fig. 1, lattice parameter $a$ decreases linearly with increasing $x$. Similar behavior has been observed for the $Ba_{1-x}K_xBiO_3$ system.[11] In an octahedral environment, the ionic size of $K^+$ or $Rb^+$ is slightly larger than that of $Ba^{2+}$, while the size of $Bi^{5+}$ is considerably smaller than that of $Bi^{3+}$. The Rb

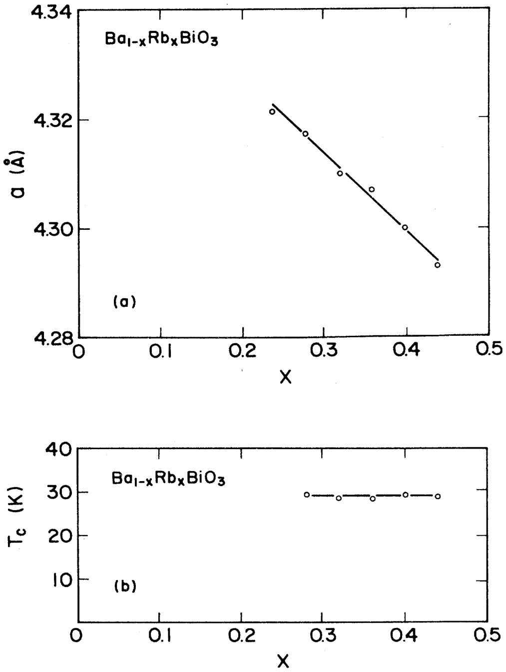

FIG. 1. Cubic lattice parameter $a$ and critical temperature $T_c$ for $Ba_{1-x}Rb_xBiO_3$ as a function of Rb concentration $x$. (a) Room-temperature $a$ values are plotted. (b) $T_c$ values are obtained from $M(T)$ measurements.

or K substitution increases the apparent $Bi^{5+}/Bi^{3+}$ ratio. Thus, the ionic-radius relation can account for the change in lattice parameter *a* with Rb or K concentration. The semiconducting parent-compound $BaBiO_3$ has a monoclinic distorted perovskite structure consisting of two distinct Bi—O bond lengths.[19] X-ray-diffraction patterns indicate that $Ba_{1-x}Rb_xBiO_3$ in the $x < 0.24$ range has a lower symmetry structure related with $BaBiO_3$. For $x > 0.48$, the $RbBiO_2$ phase appears in the diffraction data. The phase relation in the present system is similar to the situation reported for the $Ba_{1-x}K_xBiO_3$ system.[11,13,20] A large energy gap in $BaBiO_3$ is interpreted in terms of the commensurate charge-density-wave (CDW) instability.[19] The structural phase transition in $Ba_{1-x}Rb_xBiO_3$ from monoclinic to cubic symmetry seems to be accompanied by the suppression of the CDW.

Magnetization measurements on powder samples were performed using a commercial superconducting quantum interference device (SQUID) magnetometer. The zero-field-cooled (ZFC) magnetization was determined by warming the sample in a field of 10 Oe after cooling to 4.2 K in zero field. The field-cooled (FC) magnetization was obtained by cooling with the applied field. As indicated in Fig. 2, both ZFC and FC curves for $Ba_{0.6}Rb_{0.4}BiO_3$ yield $T_c = 29$ K. Schneemeyer *et al.*[13] reported that the highest $T_c$ value is 30.5 K in the $Ba_{1-x}K_xBiO_3$ system. The Rb/K mass ratio may give rise to the slight difference in $T_c$ between $Ba_{1-x}K_xBiO_3$ and $Ba_{1-x}Rb_xBiO_3$. The FC magnetization observed in the $0.28 \leq x \leq 0.44$ range corresponds to 10–45% of a full Meissner effect, indicating bulk superconductivity in this material. For lower Rb-content samples the diamagnetic signal at 4.2 K decreases sharply with decreasing *x*. At $x = 0.12$ the magnetization indicates 0.1% of perfect diamagnetism. This is due to concentration fluctuation in a fractional part of the sample. Thus, the present results lead to the conclusion that the superconductivity in the $Ba_{1-x}Rb_xBiO_3$ system exists in the $0.28 \leq x \leq 0.44$ range, where the room-temperature crystal structure belongs to the cubic phase. A similar situation[11] has been reported for the K-substituted material. Note that in Fig. 1(b) the $T_c$ values remain constant in the $0.28 \leq x \leq 0.44$ range. This suggests that the $T_c$ value is independent of hole concentration in $Ba_{1-x}Rb_xBiO_3$.

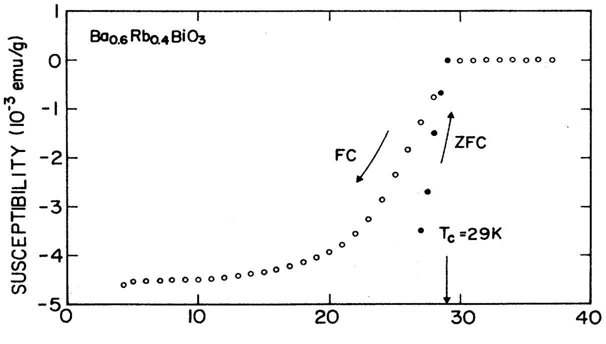

FIG. 2. Magnetization *M* at $H = 10$ Oe as a function of temperature for $Ba_{0.6}Rb_{0.4}BiO_3$. The solid circles refer to FC data, and the open circles refer to ZFC data.

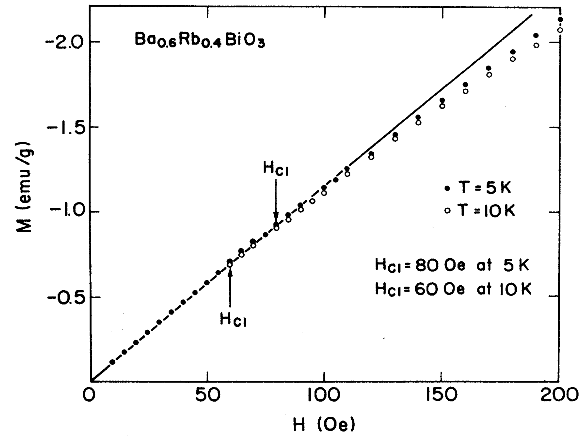

FIG. 3. Magnetization curve for $Ba_{0.6}Rb_{0.4}BiO_3$ at $T = 5$ and 10 K. $H_{c1}(T)$ is defined as the field where $M(H)$ first deviates from linearity. The straight line is a guide to the eye.

The lower critical fields $H_{c1}(T)$ were determined from the field dependence of the magnetization after cooling the sample in zero field to the desired temperature. The low-field magnetization results are plotted in Fig. 3. Here $H_{c1}(T)$ is defined as the field where the magnetization $M(H)$ first deviates from linearity. The $H_{c1}$ values are 60 Oe at 10 K and 80 Oe at 5 K. We estimate $H_{c1}(0) = 90$ Oe, on the assumption that $H_{c1}(T)$ increases linearly with decreasing temperature. The upper critical fields $H_{c2}(T)$ were obtained from constant-field magnetization measurements as a function of temperature. In Fig. 4, $T_c$ is the temperature where the constant-field magnetization starts

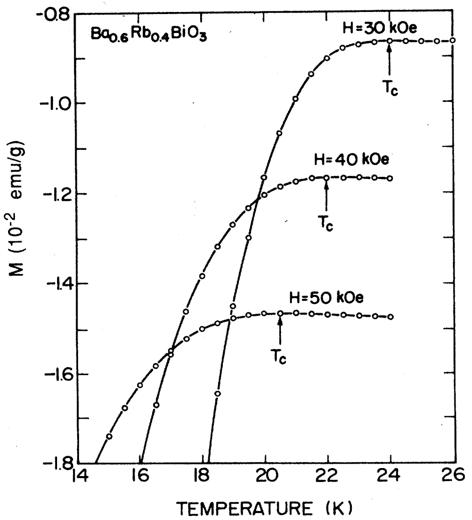

FIG. 4. Temperature dependence of magnetization *M* for $Ba_{0.6}Rb_{0.4}BiO_3$ at $H = 30$, 40, and 50 kOe. Each $T_c$ value is the temperature where $M(H)$ starts to deviate from the normal-state value.

TABLE I. Material parameters for the Bi-based superconductors. GL stands for Ginzburg-Landau.

| | $Ba_{0.6}Rb_{0.4}BiO_3$ | $Ba_{0.6}K_{0.4}BiO_3$ [a] | $BaPb_{0.75}Bi_{0.25}O_3$ [b] |
|---|---|---|---|
| $T_c$ (K) | 29 | 30 | 12 |
| $dH_{c2}/dT$ (kOe/K) | −5.9 | −5 | −5.3 |
| $H_{c1}(0)$ (Oe) | 90 | 110 | 20 |
| $H_{c2}(0)$ (kOe) | 118 | 104 | 44 |
| $H_c(0)$ (kOe) | 1.64 | 1.75 | 0.46 |
| GL $\kappa$ | 51 | 42 | 68 |
| GL $\xi(0)$ (Å) | 53 | 56 | 87 |
| GL $\lambda(0)$ (Å) | 2700 | 2350 | 5900 |
| $\gamma$ (mJ mole$^{-1}$ $K^{-2}$) | 2.4 | 2.6 | 1.1 |

[a] Reference 4.

[b] Reference 17.

to deviate from practically temperature-independent normal-state values. The upper critical fields $H_{c2}(T)$ are plotted in Fig. 5 as a function of temperature. The $dH_{c2}/dT$ slope near $T_c$ is found to be −5.9 kOe/K. We evaluate $H_{c2}(0)=118$ kOe from the relationship $H_{c2}(0)=-0.69T_c(dH_{c2}/dT)_{T_c}$, based on the Werthamer-Helfand-Hohenberg (WHH) theory[21] for the dirty-limit type-II superconductor.

The $H_{c1}(0)$ and $H_{c2}(0)$ values yield superconducting material parameters. The upper critical field $H_{c2}(0)$ is given by $H_{c2}(0)=\Phi_0/2\pi\xi^2$, where $\Phi_0$ is the flux quantum and $\xi(0)$ is the Ginzburg-Landau (GL) coherence length. Both $H_{c1}(0)$ and $H_{c2}(0)$ are expressed as $H_{c1}(0)=H_c(0)\ln\kappa/\sqrt{2}\kappa$, and $H_{c2}(0)=\sqrt{2}H_c(0)\kappa$, where $H_c(0)$ is the thermodynamic critical field, and $\kappa$ is the GL parameter. We can estimate the value for Sommerfeld parameter $\gamma=2.4$ mJ mole$^{-1}$ K$^{-2}$, based on the BCS relationship $\gamma=0.17[H_c(0)/T_c]^2$ erg cm$^{-3}$ K$^{-2}$.[22] In Table I the derived material parameters for $Ba_{0.6}Rb_{0.4}BiO_3$ are compared with those for $Ba_{0.6}K_{0.4}BiO_3$ (Ref. 4) and $BaPb_{0.75}Bi_{0.25}O_3$.[17,18] Here we estimate $H_{c2}(0)$ values from the $dH_{c2}/dT$ data using the WHH equation. Superconducting properties of the Rb- and K-substituted materials are practically described by the same material parameters. Based on the BCS relationship, the difference in $T_c$ between $Ba_{0.6}Rb_{0.4}BiO_3$ and $BaPb_{0.75}Bi_{0.25}O_3$ is partly due to the difference in the density of states near $E_F$.

Figure 6 shows normal-state susceptibility $\chi$ values for $x=0.12$, 0.28, and 0.36 as a function of temperature up to 250 K. The core diamagnetic-susceptibility $\chi_c$ is estimated to be $-2.23\times10^{-7}$ emu/g.[23] After correction for $\chi_c$, we deduce the Pauli spin susceptibility $\chi_P=0.73\times10^{-7}$ emu/g for $x=0.36$ from the observed $\chi$ value. Thus, the $\chi$ measurements yield $\gamma=2.1\pm0.3$ mJ mole$^{-1}$ K$^{-2}$, which is in good agreement with the value estimated from $H_c(0)$. The $\gamma$ values for $La_{1.85}Ba_{0.15}CuO_4$ (Ref. 24) and $YBa_2Cu_3O_{7-x}$ (Ref. 25) are reported to be 5 mJ mole$^{-1}$ K$^{-2}$. It follows that the common feature of the Bi-based superconductors is the low density of states $N(0)$ near $E_F$.

As shown in Fig. 6, there is a slight difference in $\chi$ between $x=0.12$ and $x=0.36$. This indicates that the Rb substitution exerts little influence on $N(0)$ near $E_F$ in

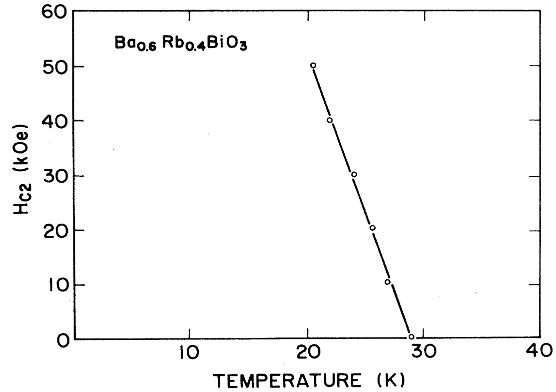

FIG. 5. Upper critical field $H_{c2}$ as a function of temperature. The data are taken from constant-field magnetization measurements as a function of temperature.

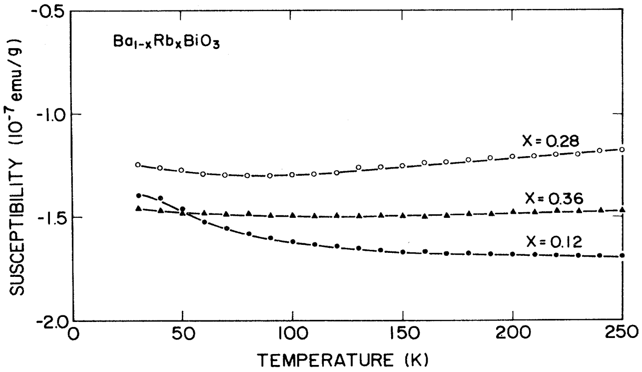

FIG. 6. Normal-state susceptibility $\chi$ in $Ba_{1-x}Rb_xBiO_3$ as a function of temperature. The sample with $x=0.12$ is nonsuperconductive material. Samples with $x=0.28$ and $x=0.38$ are superconductors with $T_c=29$ K. The diamagnetic core contribution $\chi_c$ is estimated to be $-2.23\times10^{-7}$ emu/g.

$Ba_{1-x}Rb_xBiO_3$. Mattheiss and Hamann[6] pointed out a similar behavior for $Ba_{1-x}K_xBiO_3$, based on band-structure calculations. According to their results, the antibonding Bi 6s-O 2p subbands are responsible for the conduction band near $E_F$, while the Ba 5p and K 3p orbitals participate in the nearly degenerate corelike states below $E_F$. The same explanation seems to apply to the Rb-substitution effect on $N(0)$. We expect that the mixture of Rb 4p and Ba 5p bands results in corelike states. The constant $T_c$ values in the $0.28 \leq x \leq 0.44$ range are interpreted in terms of the concentration-independent low density of states near $E_F$.

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