**Paramagnetic Meissner Effect in Superconducting Single Crystals of Ba$_{1-x}$K$_x$BiO$_3$$^{**}$

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The paramagnetic Meissner effect (PME) in the field cooled susceptibility has been observed in superconducting single crystals of Ba$_{1-x}$K$_x$BiO$_3$ using magnetometers of Quantum-Design Co.. The PME is similar to that observed in cuprates and Nb superconductors. For the Bi$_{0.63}$K$_{0.37}$BiO$_3$ crystal, the PME is observed in cooling process under the field up to 750 Oe. The PME was not found in the virgin-charged superconducting magnet. The PME is found in a superconductor with trapped flux and may arise from a remnant field, a temperature inhomogeneity near $T_c$, and a potassium-concentration inhomogeneity.

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Recently, during a few years, paramagnetic Meissner effect (PME) as an abnormal effect has been known that positive moment is observed in a positive field for a superconductor. The PME has been reported in some samples of a variety of high-$T_c$ superconductors.$^{1-7}$ It has been proposed that the effect arose in granular hole-doped cuprates from current loops with $\pi$ phase shift of the superconducting order parameter at some grain boundary junction. It is argued that such behavior would be expected to occur in a $d$-wave superconductor, but not in a conventional $s$-wave superconductor.$^8$ The PME was found in a Nb $s$-wave superconductor as well.$^5,^6$ It has been insisted that PME takes place because of a field inhomogeneity in a magnetometer.$^{5,6}$ In this paper we report new experimental results on the paramagnetic effect observed in the field cooling in superconducting single crystals of Ba$_{1-x}$K$_x$BiO$_3$ (BKBO) known as the $s$-wave superconductor.

BKBO crystals, used for the observation of PME, were synthesized by the electro-chemical method reported elsewhere.$^9$ The size of crystal I with $T_c$=31 K was 3 x 3 x 1 mm$^3$, which was obtained by abrading an original crystal 3.5 x 4 x 2 mm$^3$ with a sand paper to remove insulating phase on the surface of the crystal. The potassium concentration was analyzed as x=0.37 with the standard deviation of 0.02 at 10 points in the $ab$ plane, 0.02 at 20 points in the $ac$ plane and 0.04 at 20 points in the $bc$ plane by the electron-probe microanalysis. Color of the crystal was blue up to the inside. The $H_{c1}$ at 5 K was $\sim$750 Oe. The $\lambda(0)$ of the crystal were investigated as $\sim$5000A, respectively. In the zero-field cooled susceptibility measured at 2 Oe in Fig. 1 (a), the sharp drop at $T_c$ with transition with $\Delta T=2$ K (defined from $T_c$ to the 80% of the ZFC susceptibility at 5 K) indicates that the superconducting phase of the crystal is nearly single and homogeneous.

The susceptibilities were measured by using magnetometers of Quantum-Design Co. of MPMS-5, MPMS-5S and MPMS-2 with the MOMSR2 program. Here, the magnetometers utilize a superconducting quantum interference device (SQUID). Before measuring susceptibilities, the magnetometer of MPMS-5 was calibrated with the standard-sample of palladium and found to be operating normally in its specification. The crystal was fixed in a plastic straw in the magnetometer. Before applying a field, temperature of a crystal was increased up to 50 K above $T_c$, and again, decreased down to 5 K. The magnetometer paused for 5 minutes after setting field and temperature, and then, the zero-field cooled (ZFC) susceptibility was measured down to 5 K with decreasing temperature from the normal state. The susceptibilities are shown only up to 35 K in the following figures. The field was applied from 1 to 4000 Oe. The high resolution mode in which the magnetic field is set with a deviation within 0.2 Oe below 5000 Oe was operated. To eliminate most of remnant magnetic fields normally found in superconducting magnets, magnet cleaning in the oscillating field was carried out by dropping a field from 35,000 to 0 Oe.

Figure 1 (a)-(c) shows field dependences of FC susceptibilities observed by MPMS-5 for crystal I. Before and after measurements, in the scan-length mode of the magnetometer, values of X-axis in a SQUID-response signal did not change within the scan length. This indicates that the crystal in the straw did not move during scan. Values of ZFC susceptibilities at 5 K are different from each other to external fields, as shown in Fig. 1 (a), while those of FC ones increase with decreasing the field. The difference in the ZFC susceptibilities may be because the crystal in the magnet is affected by the inhomogeneous field $\alpha$ before being subjected to an external field, while the decrease of the FC ones may be because the crystal is subjected to $H_{ap}=H_{ex}+\alpha$ in the normal state. The paramagnetic susceptibility decreases with increasing magnetic field and changes to the diamagnetic one above $H_{tr}$~750 Oe. This field $H_{tr}$ is very large compared to those found in other crystals.$^{1-7}$ With increasing field, FC susceptibility changes to have a minimum as a function of temperature, as shown in Fig. 1 (c). With decreasing temperature near $T_c$ the FC susceptibilities below 16 Oe exhibit rapid paramagnetic increase, while the susceptibilities from 32 to 750 Oe show only a very little diamagnetic decrease, and then, again, the paramagnetic increase, as shown in inset of Fig. 1 (b).
This phenomenon was also observed in crystals with a large $\Delta T$ and in a relatively strong magnetic field. Furthermore, because surfaces of crystal I were abraded as mentioned above, PME cannot be interpreted as an impurity effect on the surface. Decrease of the paramagnetic moment at 5 K is approximately proportional to the logarithm of the inverse field; $\Delta M = A ln(1/H)$, as shown in Fig. 2. The moment of 1 Oe may be unstable in MPMS-5. The PME is similar to those observed in cuprate and Nb superconductors.\textsuperscript{1–7}

Figure 3 shows FC and ZFC susceptibilities observed by MPMS-5 for another crystal II with $T_c=29$ K. The paramagnetic susceptibility with increasing temperature after cooling in the field nearly coincides with one with decreasing temperature in the field. The transition field from paramagnetic susceptibility to diamagnetic one is $H_{tr} = 20$ Oe. Crystal II was ground to powder particles of sizes of $1 \mu m$ order and PME was still observed with the transition field $H_{tr} \approx 12$ Oe. Thus, PME may not arise from a temperature inhomogeneity because the inhomogeneity might be negligibly small for particles of a size of $1 \mu m$. The decrease of $H_{tr}$ may be due to the decreased pinning effect produced by change from the crystal to powder.

To investigate the phenomenon of the flux trap, the field dependence of the moment was measured for the crystal I placed parallel to the direction of the field ($H \perp c$-axis) with the MPMS-5S, as shown in Fig. 4. The moment in field cooling is less than that measured at $H \parallel c$-axis, which may be due to the demagnetization effect. During measuring the FC susceptibility at $H_{ex} = 5$ Oe, the external field was dropped to zero Oe at 5 K and then the moment was measured up to 40 K with increasing temperature in zero field. The paramagnetic moment increased largely. The flux was trapped. This is a ferromagnetic phenomenon by flux trap. The field inhomogeneity as a field variation in the scan length of 3 cm was not observed by measuring the field by using a Hall sensor. In measuring PME, it is independent of measurement methods, in which a sample is fixed or moved in a magnetometer, a temperature inhomogeneity near $T$ and in a relatively strong magnetic field. Furthermore, because surfaces of crystal I were abraded as mentioned above, PME cannot be interpreted as an impurity effect on the surface. Decrease of the paramagnetic moment at 5 K is approximately proportional to the logarithm of the inverse field; $\Delta M = A ln(1/H)$, as shown in Fig. 2. The moment of 1 Oe may be unstable in MPMS-5. The PME is similar to those observed in cuprate and Nb superconductors.\textsuperscript{1–7}

Even if the FC susceptibility in trapped superconductors is observed as diamagnetism, there exists evidence of the paramagnetic effect.

In conclusion, PME, which was found in the BKBO superconductor of s-wave type, cannot be interpreted as the Josephson-$\pi$ junction. The PME may arise from a remnant field trapped in a superconducting magnet in a magnetometer, a temperature inhomogeneity near $T_c$, and a potassium-concentration inhomogeneity.

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FIG. 1. For crystal I, (a) ZFC and FC susceptibilities at external fields of 1 to 11 Oe, (b) FC susceptibilities at external fields of 16 to 180 Oe, and (c) FC susceptibilities at external fields of 350 to 4000 Oe. Inset of Fig. 1 (b), FC susceptibilities near $T_c$ at external fields of 11 to 350 Oe for crystal I.

FIG. 2. Paramagnetic moment vs magnetic field at 5 K for crystal I.

FIG. 3. Field dependence of ZFC and FC susceptibilities for crystal II.
FIG. 4. Moment vs temperature for crystal I placed the $H \perp c$-axis.