Anisotropy of superconductivity from MgB$_2$ single crystals

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Magnesium diboride (MgB$_2$) single crystals, with a maximum size of 0.5 $\times$ 0.5 $\times$ 0.02 mm$^3$, were grown by the vapor transport method in a sealed molybdenum crucible. A superconducting transition with the onset temperature of 38.6 K was confirmed by both transport and magnetization measurements. The upper critical field anisotropy ratio, $H_{c2}^{ab}(0)/H_{c2}^{c}(0)$, was estimated to be 2.6 from the magnetic field-temperature phase diagram for MgB$_2$ single crystals. © 2001 American Institute of Physics. [DOI: 10.1063/1.1413729]

Following the discovery of superconductivity in magnesium diboride MgB$_2$ at about 39 K by Akimitsu and co-workers,$^1$ other physical properties such as the B isotope effect,$^2$ the pressure effect,$^3$ and the thermodynamic properties$^4$ have also been investigated, but are limited to the measurements from polycrystalline samples. Since MgB$_2$ consists of alternating hexagonal layers of Mg atoms and graphite-like honeycomb layers of B atoms, electronic anisotropy has been predicted by theoretical calculations,$^5$–$^7$ but its explicit determination has not yet been verified due to the lack of single crystals. However, certain indirect measurements have been made to determine the anisotropy, e.g., on aligned crystallites$^8$ and c-axis oriented thin films of MgB$_2$,$^9$ the anisotropy ratio, $\gamma=H_{c2}^{ab}(0)/H_{c2}^{c}(0)$, was reported as 1.7 and 1.8–2.0, respectively. Anisotropy is an important characteristic not only for the basic understanding of this material but also for its potential applications because anisotropy strongly affects the flux pinning, critical currents, and electronic device limits. Single crystals are thus urgently required for the direct investigation of anisotropic properties. In this work, we present the single-crystal growth of MgB$_2$ using the vapor transport method.$^{10}$ Anisotropic superconducting properties were evaluated by the transport and magnetization measurements.

Because of the severe volatility of Mg and the high melting point of B, MgB$_2$ single crystals were grown in a closed system. A total 2 gm mass of the starting materials of Mg (99.99%, 2–7 mm, Furuuchi Chemical) chips and a B (99.9%, 2–7 mm, Furuuchi Chemical) chunk, in a molar ratio of 1:1.9, was sealed inside a molybdenum crucible (internal diameter 10 mm, length 60 mm) by the electron beam welding. The molybdenum crucible was standing up in a high frequency induction furnace. The crucible was first heated to 1400 °C at a rate of 200 °C/h and kept for 2 h, then slowly cooled to 1000 °C at a rate of 5 °C/h, and finally to room temperature by switching off the power. About two dozens of thin plate single crystals with a maximum size of 0.5 $\times$ 0.5 $\times$ 0.02 mm$^3$ were obtained from the inner surface of the crucible. The morphology of single crystals, as shown in Fig. 1(a), was observed using a scanning electron microscope (SEM). The structural analysis of the crystal was carried out by an x-ray precession camera with a Mo target (no filter). The x-ray precession photograph of the crystal, shown in Fig. 1(b), clearly reveals the hexagonal crystal structure with lattice parameters $a=0.3047(1)$ nm and $c=0.3404(1)$ nm. The composition of the crystals was determined by an electron probe microanalyzer (JEOL JXA-8900R) and found to be MgB$_{1.9}$. The dc magnetic properties

FIG. 1. (a) SEM micrograph of MgB$_2$ single crystals. (b) Zero-layer x-ray precession photograph of the crystal in [0 0 1] zone axis.
were measured with a superconducting quantum interference device magnetometer (MPMS-5S, Quantum Design) at an applied field parallel to the c axis (H||c) or the ab plane (H||ab). The electrical resistivity of the sample, as a function of temperature and magnetic field, was measured with a Quantum Design PPMS-AG system using the standard four-probe ac method.

Figure 2(a) shows temperature dependence of the zero-field-cooled and field-cooled dc magnetization (M–T) curves of the single crystal under a field of 1 mT along the c axis and the ab plane. The M–T curves exhibit the same superconducting transition of $T_{C}^{\text{onset}}=38.6 \, \text{K}$ at H||c and H||ab, marked by an arrow in the inset. The magnetization of the single crystal, as a function of an applied field up to 5 T (M–H curve), was measured at several temperatures. Figure 2(b) shows the M–H curves at 5 K for applied fields up to 5 T at H||c and H||ab, indicating the characteristic curve of type-II superconductors. The differences between H||c and H||ab, in Fig. 2(a) for the volume fraction of the Meissner effect and in Fig. 2(b) for the gradient at high fields, indicate that the material is anisotropic. Figure 3 shows the temperature dependence of resistivity $\rho(T)$ from 5 to 280 K in the absence of a magnetic field. The $T_{C}^{\text{onset}}$ is 38.6 K, which is consistent with the result from the $M$–$T$ measurements. The $\rho(T)$ curve at 0 T can be well fitted by $a + bT + cT^2$ with $a = 1.332 \, \mu\Omega \, \text{cm}$, $b = 1.919 \times 10^{-2} \, \mu\Omega \, \text{cm/K}$, and $c = 1.234 \times 10^{-4} \, \mu\Omega \, \text{cm/K}^2$ for the normal state. Such resistivity behavior in the normal state is quite different from the reported $T^3$ behavior for polycrystalline samples. The insets in Fig. 3 show the magnetic field dependence of the resistivity under magnetic fields up to 9 T at H||c and H||ab. From the $M$–$H$ curves, the lower critical fields, $H_{c1}$ for H||c and H||ab, were defined as the magnetic fields where the initial slope of $M_{\text{up}}$ curve meets the extrapolated curve of $(M_{\text{up}} + M_{\text{down}})/2$. The temperature dependence of $H_{c1}$ is plotted in Fig. 4. Extrapolation of the plot to zero temperature gives the $H_{c1}^{(0)}$ and $H_{c1}^{(0)}$ values of 27.2 mT and 38.4 mT, respectively. The upper critical fields, $H_{c2}$ for H||c and H||ab, were determined using the resistive onset temperature from the insets of Fig. 3 and also plotted as a function of temperature in the Fig. 4. The $H_{c2}(T)$ curves for H||c and H||ab show a linear behavior for temperatures far from the $T_C$. Therefore, a linear extrapolation to zero temperature gives the $H_{c2}^{(0)}$ and $H_{c2}^{(0)}$ values of 9.2 T and 25.5 T, respectively. Assuming the dirty limit of the type-II superconductor, the $H_{c2}^{(0)}$ value is expressed as $\mu_0 H_{c2}^{(0)}$.

FIG. 2. Magnetic properties of the MgB$_2$ single crystal (corrected by the demagnetization effect). (a) Magnetization as a function of temperature after cooling under zero field and under a field of 1 mT at H||c and H||ab. The inset shows the enlarger between 34 and 40 K, showing the same superconducting transition of $T_{C}^{\text{onset}}=38.6 \, \text{K}$ at H||c and H||ab. (b) Magnetization as a function of applied fields up to 5 T at 5 K for H||c and H||ab.

FIG. 3. Resistivity of the single crystal as a function of temperature at 0 T. The resistivity as a function of temperature and magnetic fields up to 9 T at H||c and H||ab are given in upper and lower insets, respectively.

FIG. 4. Magnetic field-temperature phase diagram for the MgB$_2$ single crystal obtained from our transport and magnetization experiments, showing the temperature dependence of $H_{c1}$ and $H_{c2}$ at H||c and H||ab.
=0.7\mu_0T_C(-dH_c/dT)T_C$ and thus, $H_c^\parallel(0)$ and $H_c^{ab}(0)$ are found to be 7.7 T and 19.8 T, respectively. The present value of $H_c^{ab}(0)$ in MgB$_2$ single crystals is comparable to that estimated from the high-pressure sintered polycrystalline sample. Using the anisotropic Ginzburg–Landau (GL) formulas, $H_c^\parallel^T = \phi_0/(2\pi\xi_c^\parallel(0))$ and $H_c^{ab} = \phi_0/(2\pi\xi_{ab}\xi_c^\parallel)$, the GL coherence lengths $\xi_c^\parallel(0)$ and $\xi_{ab}(0)$ at zero temperature were calculated to be 2.5 nm and 6.5 nm, respectively. These values of $\xi_c^\parallel(0)$ and $\xi_{ab}(0)$ are larger than the typical values (1–2 nm) observed for high-temperature superconductors (HTS). For the upper critical field $H_{c2}$, the anisotropy ratio $\gamma = H_{c2}^{ab}(0)/H_{c2}^\parallel(0)$ was estimated to be 2.6, implying an anisotropy of the coherence length $\xi_{ab}(0)/\xi_c^\parallel(0) \approx 2.6$ and a mass anisotropy ratio $m_{ab}/m_c \approx 0.15$. This value of $\gamma$ is higher than the reported values of 1.7 for the aligned MgB$_2$ crystallites$^8$ and 1.8–2.0 for the c-axis oriented MgB$_2$ thin films.$^9$

In summary, we have grown the MgB$_2$ single crystals by the vapor transport method. A superconducting transition with the onset temperature of 38.6 K was confirmed through the transport and magnetization measurements. The upper critical field anisotropy ratio, $\gamma = H_{c2}^{ab}(0)/H_{c2}^\parallel(0)$ of 2.6, was estimated from the magnetic field-temperature phase diagram. The observed anisotropy is much smaller compared to the values observed for HTS and graphite intercalation superconductors,$^{13}$ which suggests that this superconductor is a promising material for applications.

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