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Ambient-pressure synthesis of single-crystal MgB$_2$ and their superconducting anisotropy

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We synthesized single crystalline MgB$_2$ under ambient pressure by using conventional materials and equipment. The single crystals of MgB$_2$ were of good quality, where the crystal structure refinements were successfully converged with $R=0.020$. The measurements of the magnetic properties yielded a sharp superconducting transition at 38 K with transition width $\Delta T_c=0.8$ K. The upper critical field for applied field parallel to the ab plane ($H_{c1}^{ab}$) reveals a positive curvature, while $H_{c2}$ parallel to the c axis ($H_{c2}^c$) increases linearly in temperature dependence, which yields a temperature dependence of the superconducting anisotropy ratio of $\gamma=H_{c1}^{ab}/H_{c2}^c$ with $\gamma\sim1$ near $T_c$ and 4.0 at 25 K.


I. INTRODUCTION

The recent discovery of superconductivity at 39 K in magnesium diboride MgB$_2$ (Ref. 1) has attracted great scientific interest because of the highest $T_c$ among conventional metals and intermetallic compounds. Several experiments indicated phonon-mediated $s$-wave BCS superconductivity$^{2,3}$ and the appearance of a double energy gap was predicted.$^{4,5}$ Specific heat$^6$ and spectroscopic$^7$ measurements, scanning tunneling spectroscopy,$^8,9$ gave evidence of this prediction. However, several key parameters such as the upper critical fields $H_{c2}$ and their anisotropy ratio $\gamma$, the magnetic penetration depth $\lambda$, the coherence length $\xi$ and Ginzburg-Landau parameter $\kappa$ are not well established because of the difficulty of growing high quality MgB$_2$ single crystals.

In particular, the anisotropy ratio $\gamma=H_{c1}^{ab}/H_{c2}^c$ is important to characterize superconducting properties and for applications of MgB$_2$. Here $H_{c1}^{ab}$ and $H_{c2}^c$ are the in-plane and out-of-plane upper critical fields, respectively. The reported $\gamma$ values vary widely depending on the measurement methods or on the sample types. The values determined from resistivity on polycrystals,$^{10}$ aligned crystallites,$^{11}$ c-axis oriented films,$^{12-14}$ and single crystals$^{15-23}$ have been reported to be 6–9, 1.7, 1.3–2, and 2.6–3, respectively.

So far, there have been several reports on superconducting properties in MgB$_2$ single crystals.$^{15,17,18,24}$ Most of these crystals were synthesized under high pressure, typically 5 GPa, with high pressure facilities. Shapes of crystals grown under high pressure are mostly irregular, so that it is almost impossible to recognize the correspondence between the crystal shapes and crystallographic axes. This causes experimental difficulties for measurements on anisotropic properties.

In this paper, we report on a method to grow a single crystal under ambient pressure, which does not require special equipments. Then we characterize the crystals in various ways. The grown crystals shows good crystalographic qualities compared with crystals grown under high pressure in the literature.$^{15,24}$ and the correspondence between sample edges and crystallographic axis is not hard to recognize. Using these crystals, we investigated the superconducting properties through magnetization measurements, and found that the anisotropy parameter $\gamma$ of $H_{c2}$ strongly depends on temperature, in particular just below $T_c$.

II. AMBIENT PRESSURE SYNTHESIS AND CHARACTERIZATION

The single crystals were grown in the stainless (SUS304) tube. Typical dimensions of stainless tubes are 32, 1.5, and 110 mm for the outer diameter, the wall thickness, and the length, respectively. The inner surface of the tube was sealed by Mo sheet (99.95%, Nilaco Co.) with the size of 0.05

![Image](http://example.com/image.png)

FIG. 1. (a) SEM image of a MgB$_2$ single crystal with a size of about 100 $\mu$m. (b) X-ray precession photograph of the single crystal.
TABLE I. Structural parameters of single crystals. Lattice constants: $a = b = 3.0863(4)$ Å, $c = 3.5178(4)$ Å. Agreement factors: $R = 0.020$, $R_w = 0.027$ ($w$ = weight).

<table>
<thead>
<tr>
<th>Atom</th>
<th>atomic orientation</th>
<th>$U_{11}$ (Å$^2$)</th>
<th>$U_{33}$ (Å$^2$)</th>
<th>$B_{eq}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>(0.0,0)</td>
<td>0.0078(2)</td>
<td>0.0054(2)</td>
<td>0.382(2)</td>
</tr>
<tr>
<td>B</td>
<td>(1/3,2/3,1/2)</td>
<td>0.0068(2)</td>
<td>0.0058(2)</td>
<td>0.371(2)</td>
</tr>
</tbody>
</table>

$\times 100 \times 200$ mm$^3$ to avoid direct reaction between the container materials and Mg/B materials. One end of the SUS304 tube was pressed with a vise and sealed in an Ar gas atmosphere by arc welding. The starting materials of a B (99.9%, Furuuchi Chemical Co.) chunk with the size of 3–5 mm and a Mg (99.99%, Furuya Metal Co.) chunk, which was cut out with the size of about 1 cm$^3$ from Mg block, were filled inside the tube. Then the other end of the tube was pressed with a vise and sealed in an Ar gas atmosphere by arc welding. The crystals were obtained about 100–300 μm, which had a partly hexagonal shape with a shiny golden color when observed under an optical microscope.

The single crystal images observed by a scanning electron microscope (SEM) is shown in Fig. 1(a). The crystals were found to have very flat surfaces. The structural analysis was carried out using a x-ray precession camera, a four-circle diffractometer, and a transmission electron microscope (TEM). The x-ray precession photograph indicated that the crystal has a hexagonal structure, as shown in Fig. 1(b). The diffraction data were collected by using graphite monochromated MoK$_\alpha$ radiation at room temperature, and refined by the least-square procedure using 86 reflections as the average of the measured 866 reflections. Finally, we obtained structural the parameters as shown in Table I.

To confirm the structure of the MgB$_2$ phase, we took a plane view of the high resolution transmission electron microscope (HRTEM) images and electron diffraction patterns in selected areas for beam directions of [110] and [001], as shown in Fig. 2, which indicated an atomic arrangement with the P6$_3$mm cell of MgB$_2$. From the left hand side of Fig. 2, we recognize two kind of layers with different spot sizes alternately stacking along the $c$ axis. Neither extra spots nor streaks were found, indicating that the crystal is of high quality.

### III. Anisotropy of the Upper Critical Field

The temperature dependence of the magnetization curve was measured at 1 mT along the $c$ axis and the $ab$ plane by a superconducting quantum interference device magnetometer. Figure 3 represent the results of magnetization measurements for the MgB$_2$ single crystal. It shows the $M(T)$ curves in the zero-field-cooling and field-cooling modes. The onset of superconducting transition was obtained at $T_c = 38$ K, with transition widths $\Delta T_c = 0.8$ K both for $H \parallel ab$ and for $H \parallel c$, indicating the high quality of the samples, where $\parallel ab(\parallel c)$ denotes the field $H$ perpendicular (parallel) to the $c$ axis, respectively. The transition temperatures are slightly lower than $T_c$ of polycrystalline specimens ($\approx 39$ K), as well as those of single crystals described in previous results. The suppression of $T_c$ was considered to be due to impurity contamination from container materials (BN, Mo, and Nb). In order to check the contamination, we per-
formed a qualitative analysis by an electron probe microanalyzer (EPMA). As a result, no contamination from our container elements (Mo, Fe, Ni, and Co) was detected within a 0.1% accuracy.

Figure 4 shows the magnetic hysteresis curves $M(H)$ at 5 K for applied fields up to 2 T for $H_{ab}$ and for $H_{c}$, indicating the characteristic curve of type-II superconductors with very small hysteresis loops. This implies that the single crystal has slight pinning effects, indicating pure single crystals with high quality.

Figure 5 shows the temperature dependence of magnetization $M(T)$ on warming after field cooling of the sample for (a) $H_{ab}$ and (b) $H_{c}$ in a magnetic field up to 2.5 T. The superconducting transition shifts to lower temperatures as the field is increased. The superconducting transition temperatures in finite fields are determined by extrapolating the negative part of the $M(T)$ curve linearly and by finding the crossing point to the horizontal line extended from the normal state. Using this criterion, the upper critical fields of MgB$_2$ for applied fields $H_{ab}$ and $H_{c}$ are obtained, as shown in Fig. 6(a). It is seen that $H_{ab}^{ab}$ shows a positive curvature in the temperature dependence near $T_c$, and then rises rapidly at lower temperatures. In contrast, $H_{c}^{ab}$ increases linearly with decreasing temperature. These temperature dependences of $H_{c}^{ab}$ have also been observed in MgB$_2$ single crystals by Lyard et al.\textsuperscript{23} and were thought to be a characteristic feature of layered superconductors such as NbSe$_2$.\textsuperscript{26} Therefore, the anisotropy ratio $\gamma=H_{c}^{ab}/H_{c}^{ab}$ is found to be temperature dependent, as displayed in Fig. 6(b). It increases from about 1 near $T_c$ to 4.0 at 25 K. The extrapolation of $H_{ab}^{ab}$ and $H_{c}^{ab}$ lines to the zero temperature axis yields $H_{ab}^{ab}(0)\sim 13.6$ T and $H_{c}^{ab}(0)\sim 3.4$ T, with $\gamma \sim 4.0$. Using the Ginzburg-Landau equation $H_{c}^{ab} = \Phi_0/(2\pi\xi^2)$, the coherence lengths $\xi$ were

![Image]

**TABLE II.** Comparison of physical parameters with single crystals prepared by different methods.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Our sample</th>
<th>References</th>
<th>References</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>3.0863(4)</td>
<td>3.085(1)</td>
<td>3.085(5)</td>
<td>3.047(1)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>3.5178(4)</td>
<td>3.518(2)</td>
<td>3.520(5)</td>
<td>3.404(1)</td>
</tr>
<tr>
<td>$R$</td>
<td>0.020</td>
<td>0.015–0.020</td>
<td>0.018</td>
<td>0.018</td>
</tr>
<tr>
<td>$R_w$</td>
<td>0.027</td>
<td>0.015–0.020</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>$T_c$ (K)</td>
<td>38</td>
<td>38–39</td>
<td>38.1–38.3</td>
<td>39</td>
</tr>
<tr>
<td>$H_{ab}^{ab}(0)$ (T)</td>
<td>13.6</td>
<td>14.5,\textsuperscript{a} 23\textsuperscript{b}</td>
<td>21–22</td>
<td>19.8</td>
</tr>
<tr>
<td>$H_{c}^{ab}(0)$ (T)</td>
<td>3.4</td>
<td>3.18,\textsuperscript{a} 3.1\textsuperscript{b}</td>
<td>7.0–7.5</td>
<td>7.7</td>
</tr>
<tr>
<td>$g(T)$</td>
<td>$1(T_c)$ -4.0 (25 K)</td>
<td>$1(T_c)$-4.2 (22 K)\textsuperscript{a}, 2.8 (35 K)-6 (15 K)\textsuperscript{b}</td>
<td>$2.2(T_c)$-3 (30 K)</td>
<td>2.6 (0 K)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Values determined from the magnetic measurement.

\textsuperscript{b}Values determined from the magnetic torque measurement.
yielded to be $\xi_{ab}(0) \sim 10$ nm and $\xi_c(0) \sim 3$ nm. These values are similar to the previous results obtained from magnetic measurements on powder samples$^{15–18,10,11,29}$ and the values determined from the calculation using the two band model,$^{28}$ but do not agree with the reported $\gamma$-values determined from resistivity measurements on bulk samples$^{15–18,10,11,29}$ and $c$-axis-oriented films,$^{12–14}$ which are around 1.1 to 3, as shown in Table II.

IV. CONCLUSION

We have succeeded in synthesizing the single crystals under ambient pressure. So far the single crystals were produced by using special high pressure facilities. The synthesized single crystals are found to be of good quality ($R = 0.020, R_w = 0.027$) judging from the structural analysis standard.

We measured the magnetic properties of single crystalline MgB$_2$, and found a marked anisotropy; $H^a_{c2}$ reveals a positive curvature while $H^c_{c2}$ increases linearly in the temperature dependence. The anisotropy ratio $\gamma = H^a_{c2}/H^c_{c2}$ of the upper critical field is shown to be increased from about 1 near $T_c$ to 4.0 at 25 K.

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