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Crystal growth of the two-dimensional spin gap system $SrCu_2(BO_3)_2$

H. Kageyama, K. Onizuka, T. Yamauchi, Y. Ueda*

Material Design and Characterization Laboratory, The Institute for Solid State Physics, The University of Tokyo, Roppongi 7-22-1, Minato-ku, Tokyo 106-866, Japan

Abstract

Our high-quality large single crystals of $SrCu_2(BO_3)_2$ have been successfully grown by a travelling solvent floating zone (TSFZ) method using $LiBO_2$ as a solvent. We present the growth condition and the result of the temperature-dependent magnetic susceptibilities measured along the directions parallel and perpendicular to the tetragonal c-axis. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

For theorists in the field of condensed matter physics, models achieving an exact dimer ground state have been one of the interesting subjects [1,2]. However, in spite of vigorous efforts of experimentalists, no materials realizing the models have been found. Quite recently, it was found that $SrCu_2(BO_3)_2$ is a two-dimensional spin gap system with the exact dimer ground state [3,4], which indeed realizes the Shastry–Sutherland model [5,6]. This cuprate crystallizes in space group $I\bar{4}2m$ with a unit cell of dimensions: $a = 8.995$ Å, $c = 6.649$ Å, and $V = 537.9$ Å^3. The structure is

characterized by a novel two-dimensional magnetic network of the Cu^{2+} ions with $S = \frac{1}{2}$ (topologically equivalent to the Shastry–Sutherland lattice), in which neighboring Cu^{2+}–Cu^{2+} dimers connect orthogonally. Furthermore, quantized plateaux at $\frac{1}{4}$ and $\frac{1}{8}$ of the full Cu^{2+} moment were observed in the magnetization. The previous experiments, however, were performed using a polycrystal so that large single crystals of high quality have been indispensable for further elucidation of the intrinsic nature of the ground state as well as the excited states. Although Smith and Keszler obtained single crystals by a flux method using $LiBO_2$ [7], the crystal size (0.20 mm × 0.08 mm × 0.03 mm) is not enough for more sophisticated physical measurements. To achieve this goal, we employed a vertical travelling solvent floating zone (TSFZ) method using $LiBO_2$ as a solvent. Consequently, we obtained sufficiently

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*Corresponding author. Tel.: + 81-3-3478-8459; fax: + 81-3-3478-8459.

E-mail address: yueda@kodama.issp.u-tokyo.ac.jp (Y. Ueda)

large single crystals, and investigated the magnetic properties using the obtained crystals.

2. Experimental procedure

Since $SrCu_2(BO_3)_2$ melts incongruently in air at a peritectic melting point of $970°C$, a solution-growth technique with the aid of an appropriate solvent is necessary for the purpose of its crystal growth. Polycrystalline $SrCu_2(BO_3)_2$ was prepared by a solid state reaction. Starting materials of $SrCO_3$, CuO and B_2O_3 with 99.99% purity were mixed, ground, followed by heat treatment at $900°C$ in flowing oxygen for 1 week with several intermediate grindings. The resulting blue powder was isostatically water-pressed under $400 \, kg/cm^2$ in the form of rods (6–10 mm in diameter and ~ 100 mm in length), yielding densities of about 70%. The rods were subsequently sintered at $850°C$ for 1 day under oxygen flow. We also prepared a solvent disk (2–3 mm in thickness) composed of a mixture of $LiBO_2$ and $SrCu_2(BO_3)_2$ in the weight ratio of 1 : 3.

The crystal growth was carried out using FZ-T10000N 10 KW high-pressure type (Crystal System. Inc.) with four halogen lamps as heat sources. The solvent disk was placed between the upper and the lower rods. By gradually increasing the lamp power, the solvent disk was molten. Immediately, the upper rod was moved downwards in order to establish a floating zone between the lower and the upper rods. Growth rates were 0.3–1.0 mm/h and both rods were rotated at about 10 rpm in opposite directions to secure the liquid homogeneity as well as the homogeneous temperature distribution within the liquid zone. Only oxygen gas (1 atm, 99.99%) was allowed to flow during the growth process.

The X-ray powder diffraction pattern indicated a single-phase product. Single crystallinity of the grown material was checked by means of Laue X-ray back-reflection. The temperature T dependence of the magnetic susceptibility was measured in the magnetic field of 1.0 T, using a superconducting quantum interference device (SQUID) magneto-meter (Quantum Design, MPMS) in a T range, $2 \, K < T < 350 \, K$.

3. Result and discussion

We have succeeded in growing crystals of $SrCu_2(BO_3)_2$. The crystals obtained are dark blue and easily cleaved along the tetragonal ab plane as confirmed by Laue X-ray back-reflection. Fig. 1(a) shows a photo of a typical crystal rod (6 mm in diameter) containing a single domain 43 mm long, where the feed rod with 6 mm diameter and the solvent $LiBO_2$ with 0.05 g weight were applied to grow this crystal. In Fig. 1(b), we show a single domain (6 mm × 6 mm × 3 mm) with the glossy cleavage plane, i.e., the ab plane. It was found that the crystal size is entirely dependent on the crystallization rates. When a crystallization rate was
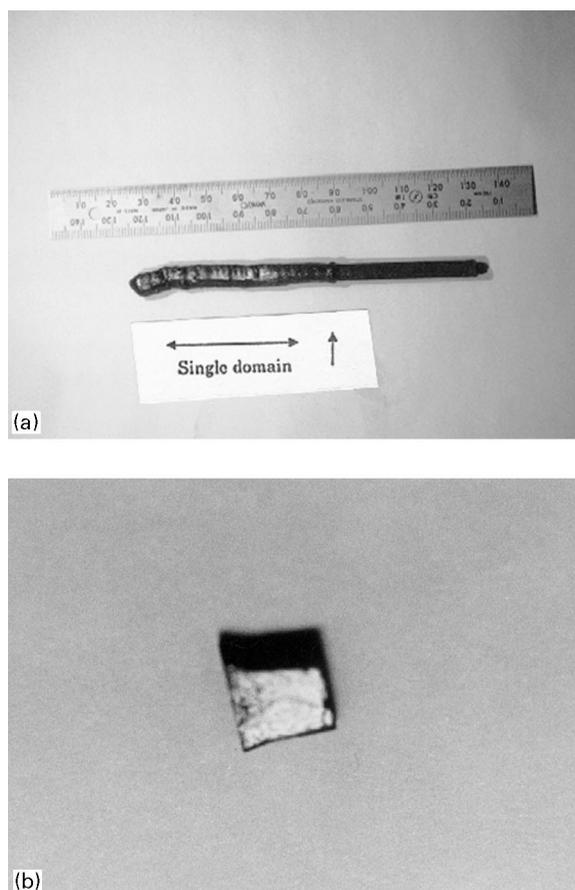

Fig. 1. The representative photos of a crystal rod (a) and a single domain (b) of $SrCu_2(BO_3)_2$. The upward arrow in (a) indicates the starting point of the crystal growth.

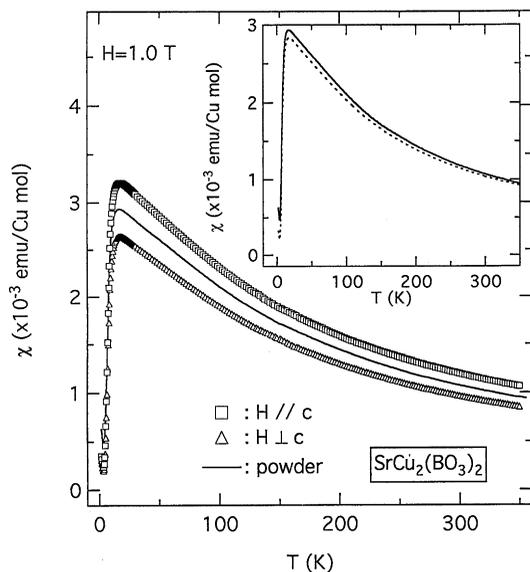Fig. 2. The temperature-dependent magnetic susceptibilities of $SrCu_2(BO_3)_2$, $\chi_{||}$ ($\square$) and $\chi_{\perp}$ ($\triangle$). The solid line denotes the susceptibility for the powdered sample [3]. Inset: the susceptibility of the powdered sample (solid) and the calculated isotropic susceptibility of the crystal (broken).

1.0 mm/h, the crystal grew easily along the *ab* plane (typically 5 mm × 5 mm), while the growth along the *c*-axis was exceedingly small (less than 0.5 mm). In addition, some Laue photos taken along the *c*-axis have several weak spots around a strong spot, indicating some kind of imperfections in the single crystal.

Accordingly, a slower growth rate of 0.5 mm/h was then employed. As a result, the crystals became monodomain after several centimeters of growth as seen in Fig. 1(a), and the Laue-photo analysis has proven a single crystal product without any imperfections. Since the liquid zone contains a solvent and therefore the composition is different from that of the crystal and the charge rods, we consider slow growth rates would be necessary for sufficient diffusion to take place at the solid–liquid interface.

Fig. 2 demonstrates the temperature dependence of magnetic susceptibilities of $SrCu_2(BO_3)_2$, $\chi_{||}$ and $\chi_{\perp}$, in which the magnetic field was applied parallel and perpendicular to the *c*-axis, respectively. The solid line represents the previous data for the powdered sample [3]. The difference between $\chi_{||}$ and $\chi_{\perp}$ is attributable to the anisotropic *g*-factor as

observed by electron spin resonance (ESR) [8]. At high temperatures, both $\chi_{||}$ and $\chi_{\perp}$ obey the Curie–Weiss law $\chi = Ng^2\mu_B^2 S(S+1)/[3k_B(T-\theta)]$, where N denotes Avogadro number, μ_B, the Bohr magneton, k_B, Boltzmann constant, g, the *g*-factor of the Cu^{2+} electron spin, and θ, Weiss constant. Using $S = \frac{1}{2}$ for the Cu^{2+} ion and $g_{||} = 2.28$ and $g_{\perp} = 2.07$ determined by the ESR measurement, we fitted the experimental data in the temperature range between 250 and 350 K to the above formula, and obtained $\theta = -102.5$ K together with a constant susceptibility $\chi_0 = -2.603 \times 10^{-5}$ emu/mol Cu. Shown in the inset of Fig. 2 is a comparison between the susceptibility of the powdered sample and the isotropic susceptibility ($= \frac{1}{3}\chi_{||} + \frac{2}{3}\chi_{\perp}$) of the crystal. We would like to emphasize that a Curie-like upturn below 4 K presumably coming from defects in the crystal is much smaller than that for the powdered sample, clearly showing the high quality of the present crystal.

4. Conclusion

In summary, we have grown single crystals of $SrCu_2(BO_3)_2$ by means of a TSFZ method with an image furnace using $LiBO_2$ as a solvent. The X-ray diffraction analysis and the relatively small Curie-like upturn in the low-temperature susceptibility ensure high quality of the grown crystal. Other physical measurements such as nuclear magnetic resonance, high-field magnetization, and neutron scattering using the crystals are now in progress.

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