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Field Induced Lattice Deformation in the Quantum Antiferromagnet $SrCu_2(BO_3)_2$

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The results of synchrotron X-ray diffraction by the coupled dimer compound $SrCu_2(BO_3)_2$ subjected to a pulsed high magnetic field are reported. We find the lattice constant, a, contracts with increasing magnetic field. This change in the lattice constant scales with the magnetization change. We argue that the nearest neighbor exchange interaction between Cu^{2+} spins is an antiferromagnetic one through an oxygen and its strength depends on the bond angle Cu^{2+}–O^{2-}–Cu^{2+}. The bond length between the Cu ions in a triplet becomes shorter to make the bond angle smaller and to diminish the antiferromagnetic exchange interaction. We propose this mechanism as a main source of the lattice contraction.

KEYWORDS: $SrCu_2(BO_3)_2$, synchrotron X-ray diffraction, high magnetic field, magneto-elastic coupling, exchange interaction
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Magnetic systems with a non-magnetic ground state and an energy gap to the lowest excited state, have attracted much attention in recent years. A simple example of such quantum antiferomagnets is found in a dimer, in which two $S = 1/2$ spins interact with an antiferromagnetic exchange interaction constant, J. The compound, $SrCu_2(BO_3)_2$ (abbreviated SCBO, hereafter) has a non-magnetic ground state and an energy gap as evidenced by the temperature dependence of the magnetic susceptibility and nuclear quadrupole resonance measurements.[1)] The crystal structure[2)] of SCBO allows one to discuss the magnetism based on a model with interacting dimers in two dimension.[1,3)]

A novel feature found in SCBO is the appearance of magnetization plateaux: when an external magnetic field, B, is applied, this material shows magnetization plateaux at 1/8, 1/4, and 1/3 of the saturation magnetization at low temperatures.[1,4,5)] The origin of these magnetization plateaux has been studied theoretically by several authors.[3,6–11)] With increasing magnetic field, the energy of the lowest excited state with $S^z_{\rm tot} = 1$ decreases and it becomes the ground state above a critical field, $H_{\rm c}$ ($\sim$20 T). We call this field induced triplet state a "triplet", in which each spin of a Cu^{2+} dimer has $S_z = 1/2$. As discussed by Miyahara and Ueda,[3)] this triplet is heavily localized and so an arrangement of these triplets with a unique pattern is expected to occur at each plateau phase. From a nuclear magnetic resonance (NMR) study performed on SCBO at a temperature, $T = 35$ mK, Kodama *et al.* found at least eleven distinct sites for Cu in the 1/8 plateau phase.[12)] They proposed a pattern with a rhomboid unit cell containing one triplet at the corners and seven dimers with different magnetic moments inside.

Tsujii *et al.* reported that a finite energy gap exists at $H_{\rm c}$ from their heat capacity, C_p, measurements on SCBO.[13)] Therefore, the energy level scheme is more complex than that described above.[14,15)] Nonetheless, it may be a good approximation to describe the magnetism of SCBO above $H_{\rm c}$ as a collection of the triplets. They have also found a sharp peak in C_p below 1 K at fields $27.5 \leq B \leq 33$ T and interpreted this finding as due to a freezing of the triplets.[13)]

The magnetization of SCBO changes gradually in the field regions between the plateaux.[1,4,5)] The nature of the intermediate states between the plateaux has not been fully understood. Momoi and Totsuka[9)] argued that a supersolid state will appear in the intermediate states. In recent years, extensive theoretical studies have been done on this supersolid.[16–18)] Takigawa *et al.* reported that a freezing of the triplets still exists in the intermediate state between the 1/8 and 1/4 plateaux from their NMR measurements.[19)]

In this paper, the results of synchrotron X-ray diffraction measurements by SCBO under pulsed, high magnetic fields are reported. We find that the lattice constant shrinks with increasing magnetic field. This result clearly shows a coupling of spin and lattice degrees of freedom. A spin–lattice coupling has been found in SCBO by ultrasonic experiments.[20)] Here, we report the first direct observation of the lattice distortion associated with the emergence of the triplets. We discuss the origin of the lattice distortion in an atomic level.

The compound, $SrCu_2(BO_3)_2$ has the tetragonal crystal structure (space group $I\bar{4}2m$) at room temperature and the lattice constants are $a = 8.995$ Å and $c = 6.649$ Å.[2)] The crystal structure projected onto the ab-plane is shown in Fig. 1. Copper, oxygen and boron atoms sit on a plane perpendicular to the c-axis. The Cu–O–B plane and the plane containing Sr are stacked alternately along the c-axis and we expect that the magnetic interaction between the planes is very weak. The Cu dimers coupled by J are shown by two filled circles connected by dashed line in Fig. 1. These dimers interact with the neighboring orthogonal dimers with an exchange interaction constant, J'. Writing the exchange interaction between spins $\boldsymbol{S}_i$ and $\boldsymbol{S}_j$ as, $J\boldsymbol{S}_i \cdot \boldsymbol{S}_j$, the values of the exchange constants in SCBO are, $J/k_{\rm B} = 85$ K and $J'/k_{\rm B} = 54$ K,[21)] where, $k_{\rm B}$ is the Boltzmann's constant. The value of the spin gap, Δ, is $\Delta/k_{\rm B} \simeq 35$ K.[21)]

The single crystal sample of SCBO used in this study was grown by a traveling solvent floating zone method[22)] and cut

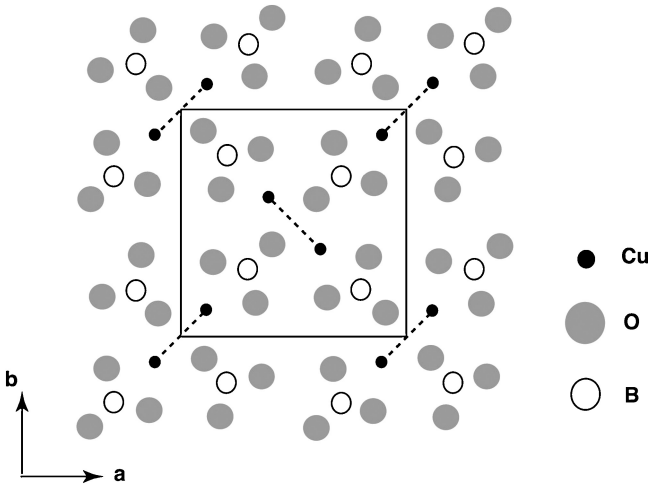

Fig. 1. The crystal structure of $SrCu_2(BO_3)_2$ projected onto the *ab*-plane. Sr atoms are omitted, for clarity.

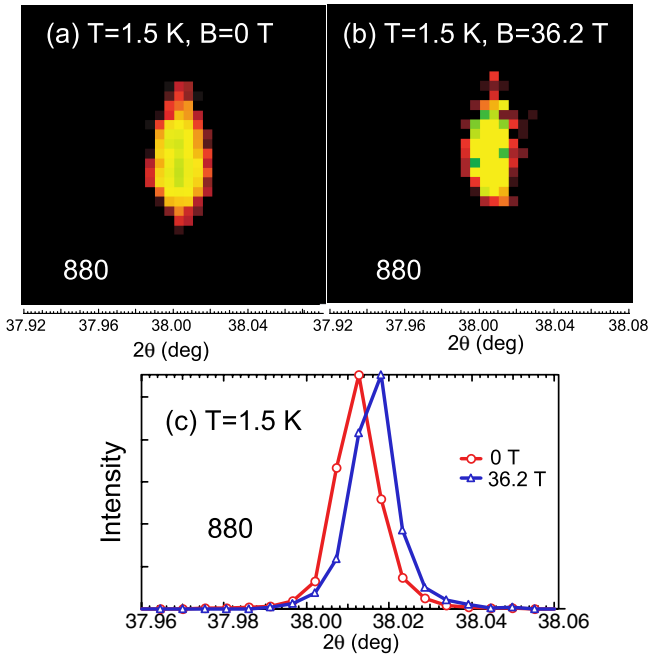

Fig. 2. (Color online) X-ray diffraction images around the (880) reciprocal lattice point in $SrCu_2(BO_3)_2$, obtained at (a) $T = 1.5\,\mathrm{K}$ and $B = 0\,\mathrm{T}$, and (b) $T = 1.5\,\mathrm{K}$ and $B = 36.2\,\mathrm{T}$. Horizontal direction in these images corresponds to the scattering angle, 2θ. (c) Diffraction profiles extracted from the images.

into a parallelepiped with dimensions $\simeq 1.5 \times 2 \times 3\,\mathrm{mm}^3$. Synchrotron X-ray diffraction measurements in pulsed, high magnetic fields were conducted at the beamline BL19LXU at SPring-8. The experimental details are given in refs. 23, 24. The single crystal was mounted with its *c*-axis vertical ($\|\boldsymbol{B}$) in a glass dewar which was inserted into the pulsed field magnet. Incident and diffracted X-ray beams were in the horizontal plane ($\perp\boldsymbol{B}$). The incident beam was tuned to 24 keV in energy by a double-Si-crystal monochromator equipped with a cryogenic cooling system.

Figures 2(a) and 2(b) show examples of the diffraction patterns obtained with the two-dimensional detector.[23)] We have measured the magnetic field and temperature dependence of the (880) and (660) Bragg points. In some cases, we have observed a splitting of the diffraction pattern, which is caused by the presence of two neighboring grains with a small angle ($\simeq 0.03^\circ$) apart. In the following, we show only the data obtained from a single grain. Figure 2(c) shows diffraction profiles extracted from the images.

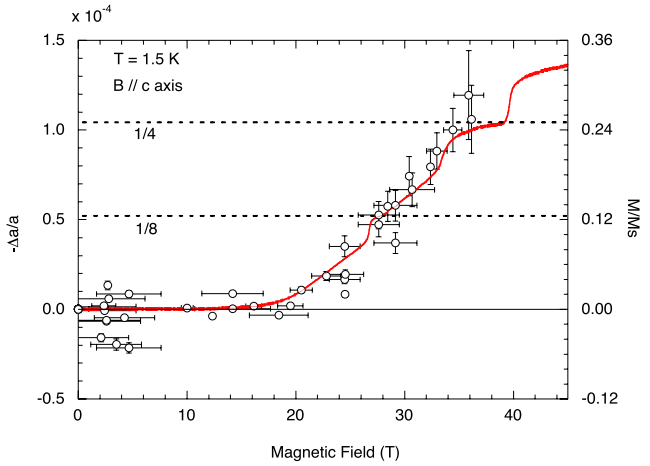

Fig. 3. (Color online) The magnetic field dependence of relative change in the lattice constant, $[a(B = 0\,\mathrm{T}) - a(B)]/a(B = 0\,\mathrm{T})$ measured at $T = 1.5\,\mathrm{K}$. Also shown is the magnetic field dependence of the magnetization relative to the saturation value, M_s (red curve). The magnetization data were taken from ref. 4. Dashed horizontal lines show the positions of the magnetization plateaux.

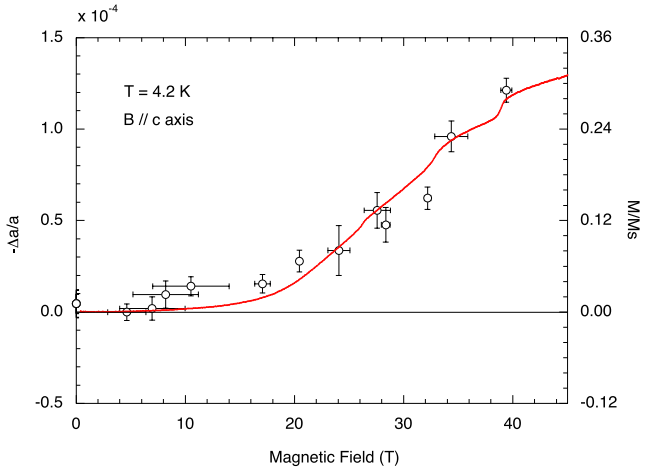

Fig. 4. (Color online) The magnetic field dependence of relative change in the lattice constant, $[a(B = 0\,\mathrm{T}) - a(B)]/a(B = 0\,\mathrm{T})$ measured at $T = 4.2\,\mathrm{K}$. Also shown is the magnetic field dependence of the magnetization relative to the saturation value (red curve).

We show in Fig. 3 the magnetic field dependence of the lattice constant, *a*, relative to its zero-field value determined from an analysis of the (880) Bragg peak. We also plot the magnetic field dependence of the magnetization, *M*, relative to the saturation value, M_s. All the data presented here were taken in an increasing magnetic field. The lattice constant is seen to decrease with increasing *B*, in coincidence with the magnetization changes. Figure 4 shows the corresponding data taken at 4.2 K obtained from an analysis of the (660) Bragg peak. Although the magnetization change at the plateaux becomes less pronounced with increasing temper-

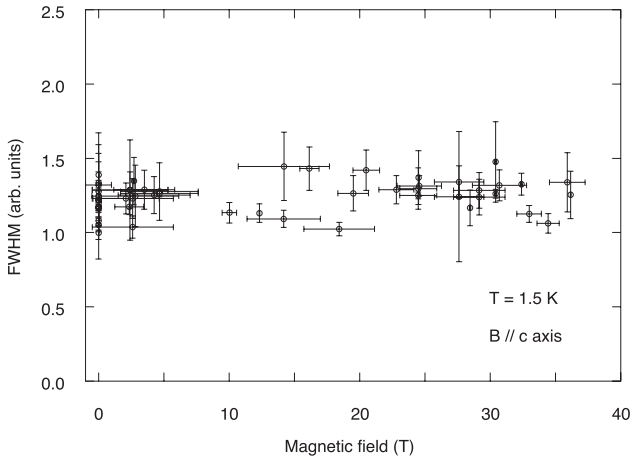

Fig. 5. The magnetic field dependence of the full width at half maximum of the (880) Bragg peak measured at $T = 1.5$ K.

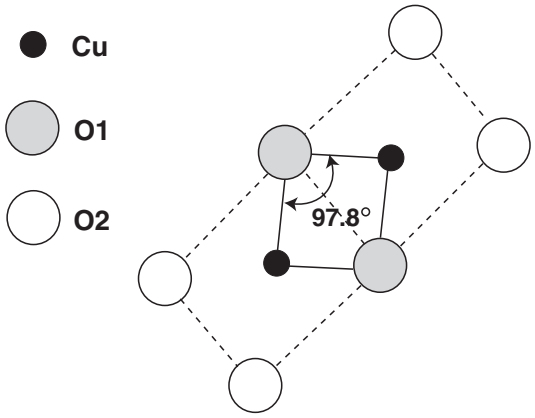

Fig. 6. The arrangement of oxygen ions around a Cu-dimer in the *ab*-plane of $SrCu_2(BO_3)_2$.

ature, the amount of the lattice distortion is essentially unchanged.

Figure 5 shows the magnetic field dependence of the radial directional full width at half maximum (FWHM) of the (880) Bragg peak. The width does not change much with magnetic field. So, we may conclude that the crystal symmetry remains unchanged with magnetic field up to 40 T.

Let us discuss the origin of the lattice distortion found in this study. The ground state of a free Cu^{2+} ion is ^2D with total orbital angular momentum, $L = 2$ and total spin, $\mathcal{S} = 1/2$. In an octahedral crystal field, the orbital states split into a triplet, $d\epsilon$, and a doublet, $d\gamma$, the latter has the lowest energy. A Cu^{2+} ion in SCBO is coordinated by four O^{2-} ions in the *ab*-plane as shown in Fig. 1. There is no anion immediate above and below the Cu^{2+} ion along the *c*-axis. In this case, the two-fold degeneracy of the $d\gamma$ state is lifted and the ground orbital state is predominantly the one with the $(x^2 - y^2)$ symmetry.

We propose the following mechanism to explain the observation. In Fig. 6 we show the arrangement of oxygen ions around a Cu-dimer in the *ab*-plane of SCBO. The nearest neighbor super-exchange interaction between Cu^{2+} spins is the one through an oxygen. The bond angle Cu–O1–Cu is 97.8°.[2] Goodenough argued that the 90° super-exchange interaction between Cu^{2+} spins is weak.[25] On the other hand, we have experimental evidence that the 180° super-exchange interaction between Cu^{2+} spins is antiferromagnetic and strong.[26,27] The increase in the bond angle from 90° will strengthen an antiferromagnetic exchange interaction.

Above H_c, triplets are induced in the sample. Then, the bond length between Cu^{2+} ions in the triplets is expected to shrink to make the bond angle smaller resulting in a weaker antiferromagnetic exchange interaction. Since Cu^{2+} has nine $3d$ electrons, which can be regarded as a one-hole system, we expect that the hole orbit with the $(x^2 - y^2)$ symmetry will attract the O2 ions to the Cu^{2+} ion. In this way, the lattice constant, *a*, becomes shorter with no detectable change in the crystal symmetry, in accordance with the observation (Figs. 3–5). The magnetization is proportional to the number of triplets in the sample and so the amount of the lattice distortion is proportional to the magnetization. We see in Figs. 3 and 4 that the field dependence of the lattice distortion is nicely correlated with that of the magnetization.

In addition to the antiferromagnetic exchange interaction discussed above, there might be a direct exchange interaction, which is considered to be ferromagnetic. We expect that the bond length between Cu^{2+} ions in the triplets will shrink to gain the ferromagnetic direct exchange interaction. So, the effect of direct exchange interaction, if present, on the lattice distortion is the same as that of the antiferromagnetic one.

Many Cu^{2+} compounds are known to exhibit lattice distortion via the Jahn–Teller effect. As explained above, the two-fold degeneracy of the $d\gamma$ state in SCBO has been lifted and further gain in energy is obtained when the neighboring O^{2-} ions move towards the Cu^{2+}. Because the lattice constant does not change at the low field region below ~25 T and begins to decrease above this field, electron spin of Cu^{2+} in the triplets must play an essential role in the lattice distortion. An electron spin couples to the lattice via the spin–orbit interaction and affects the Jahn–Teller distortion. Our observation could be explained if we would assume that the Jahn–Teller distortion was present in the triplet state and absent in the singlet state. At the moment, we have no reasoning to support this assumption.

In conclusion, we have studied the correlation between the magnetism and lattice degrees of freedom in the coupled dimer compound $SrCu_2(BO_3)_2$ in applied magnetic field by synchrotron X-ray diffraction technique. We found the lattice constant, *a*, contracts with increasing magnetic field. This change in the lattice constant scales with the magnetization change. We argued that the nearest neighbor exchange interaction between Cu^{2+} spins is the antiferromagnetic one through an oxygen and depends on the bond angle Cu^{2+}–O^{2-}–Cu^{2+}. The bond length between the Cu ions in a triplet becomes shorter to make the bond angle smaller, resulting in a weaker exchange interaction. We proposed this mechanism as a main source of the lattice contraction. It was believed that there was no chance to detect a tiny structural distortion with X-rays in high fields.[11] It is now possible to do X-ray diffraction measurements up to 40 T as demonstrated in this paper and in refs. 23, 24, and 28.

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