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Two distinct ferroelectric phases in the multiferroic *Y*-type hexaferrite $Ba_2Mg_2Fe_{12}O_{22}$

Hajime Sagayama,[1] Kouji Taniguchi,[1] Nobuyuki Abe,[1] Taka-hisa Arima,[1] Yusaku Nishikawa,[2] Shin-ichiro Yano,[2] Yusuke Kousaka,[2] Jun Akimitsu,[2] Masato Matsuura,[3] and Kazuma Hirota[3]

[1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan*

[2]*Department of Physics and Mathematics, Aoyama Gakuin University, Sagamihara, Kanagawa 229-8558, Japan*

[3]*Department of Earth and Space Science, Graduate School of Science, Osaka University, Toyonaka 560-0043, Japan*

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The magnetic phase diagram of the *Y*-type hexaferrite $Ba_2Mg_2Fe_{12}O_{22}$ has been studied using single-crystal neutron diffraction. The result indicates successive phase transitions where the magnetic modulation wave number changed discontinuously when a magnetic field is applied and the temperature is varied. For the low-temperature spin-driven ferroelectric state, we have found a sixfold structure with $\boldsymbol{q}=(0\ 0\ 1/2)$ in weak magnetic fields and a twofold structure with $\boldsymbol{q}=(0\ 0\ 3/2)$ in strong magnetic fields between which a first-order transition intervenes accompanied by a hysteresis.

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A number of studies[1–3] have been conducted on a group of materials known as multiferroics, in which electric polarization and magnetism occur simultaneously in an ordered state. Of particular interest is the fact that massive electric-magnetic effects are observed in systems where a spiral magnetic structure induces ferroelectric polarization. While these materials show potential for applications in devices, many of them require strong magnetic fields (of the order of several tesla) to produce this effect. Of the currently reported multiferroics, the *Y*-type hexaferrite $Ba_2Mg_2Fe_{12}O_{22}$ exhibits the highest controllability of ferroelectric polarization under weak magnetic fields.[4,5] Ferroelectric polarization in $Ba_2Mg_2Fe_{12}O_{22}$ is induced by applying magnetic fields perpendicular to the *c* axis and the polarization remains in a zero magnetic field. The direction of the electric polarization can be inverted by rotating an extremely weak magnetic field (20–30 mT) at 180°. The nature of changes in the spin configuration with magnetic field and temperature is an area of interest because the electric polarization is induced by magnetic ordering. However, to date, there have been no reports on this matter.

Y-type hexaferrite refers to a group of substances which can be expressed in the general form $A_2M_2Fe_{12}O_{22}$. These ferrites have a crystalline structure consisting of blocks having a spinel structure, with blocks containing *A*O laminated alternately on top of each other. The space group is a rhombohedral crystal $R\bar{3}m$,[6] and therefore each spinel layer and *A*O block is repeated three times in a practical unit cell of the hexagonal setting. Since *A* represents alkaline-earth elements and *M* represents divalent ions, such as Mg and Zn, the average valence of the Fe ion is three with oxygen positioned at the vertices of an octahedron or a tetrahedron. Although an antiferromagnetic exchange interactions occur between adjacent Fe^{3+} ions, a complex magnetic structure can be observed as a result of some of the exchange interactions competing with each other. The magnetic structures of $Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}$ have been studied using neutron diffraction.[7,8] Momozawa *et al.* considered a block L, which possesses a large effective magnetic moment μ_L, and a block S, which possesses a small effective magnetic moment μ_S, as units of the magnetic structure of this system. The Fe spins in each block are aligned approximately collinearly in the *ab* plane and form ferrimagnetic block.[7] Furthermore, in a zero magnetic field, μ_L and μ_S rotate and form a proper screw-type structure with an incommensurate (IC) period, which is determined as a function of *x* and temperature. By applying a magnetic field in a direction orthogonal to the *c* axis, the compound with $x\sim0.5$ undergoes successive magnetic transitions. Three fan-type phases are reported as intermediate phases, and a collinear ferromagnetic structure appears in a magnetic field higher than 2 T. Kimura *et al.* discovered ferroelectric polarization in a fan phase with a magnetic modulation wave number $\boldsymbol{q}=(0\ 0\ 3/2)$.[9] However, since the proposed fan structure does not break the space inversion, the mechanism which induces ferroelectric polarization is not yet known.

The magnetic structure of $Ba_2Mg_2Fe_{12}O_{22}$ has been studied only in a zero magnetic field.[10,11] At room temperature, it exhibits a ferrimagnetic structure, where μ_L and μ_S are ordered in an antiferromagnetic manner as shown in Fig. 1(a). At approximately 200 K, it undergoes a transition to a proper-screw type structure, similarly to $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$, and at 9 K the period is reported to be 1.74*c*. Ishiwata *et al.* reported an increase in magnetization along the *c* axis below 50 K and assigned a phase transition to a longitudinal conical structure. Recently, Taniguchi *et al.* and Ishiwata *et al.* independently reported the existence of ferroelectric polarization and a strong magnetoelectric effect at low temperatures.[4,5] As can be seen in Fig. 1(d), remanent electric polarization can be observed in a zero magnetic field. While electric polarization increases discontinuously when a magnetic field of 0.13 T is applied, electric polarization disappears at 3 T or greater.[5] This electric polarization can be inverted while preserving its magnitude by applying an inverted magnetic field with a strength of several dozen mT. Ishiwata *et al.* have proposed a mechanism whereby a longitudinal conical structure undergoes a transition to a transverse conical structure which has the rotation axis perpendicular to the propagation direction as opposed to the longitudinal conical spiral, resulting in ferroelectricity.[5,12] They have also inferred, based on the shape of the electric-magnetic phase diagram, that in a region with a magnetic field of 0.2–3 T, a ferroelectric phase having the same mag-

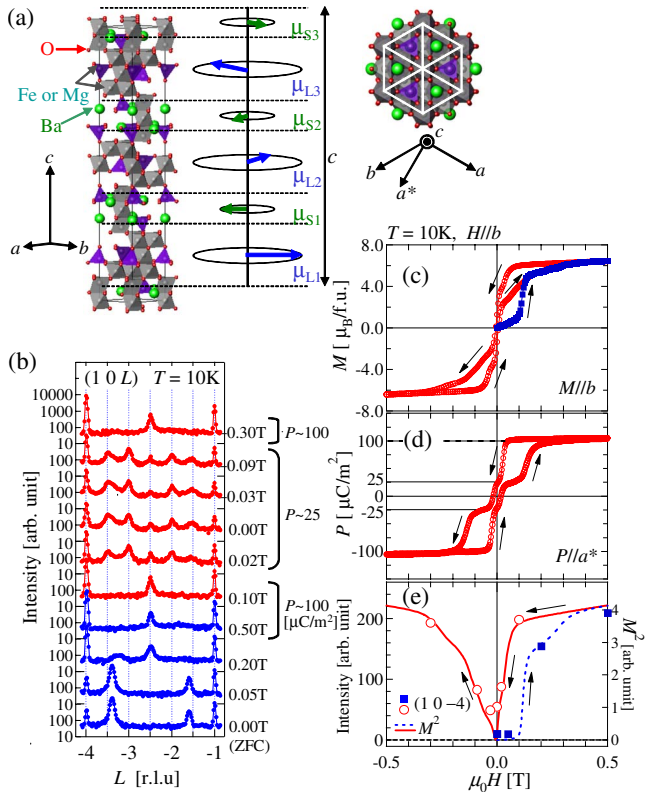

FIG. 1. (Color online) (a) Crystal structure and proper screw-type spin structure of $Ba_2Mg_2Fe_{12}O_{22}$. μ_L and μ_S denote the effective magnetic moments of blocks L and S, respectively. (b) (1 0 *L*) scan profiles in various magnetic fields at 10 K. Intensity is plotted on a logarithmic scale. A magnetic field was applied after the ZFC process. [(c) and (d)] Magnetization (*M*) and electric polarization as a function of magnetic field at 10 K. Dark (blue online) closed squares and line indicate the initial magnetization process. (e) Dependence of neutron-diffraction intensity for (1 0 −4) on the magnetic field at 10 K. Solid line indicates the square of the *M* in the corresponding processes. Dark (blue online) closed squarers and broken line indicate the initial magnetization process.

netic structure as $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ appears. However, neutron-diffraction studies have not yet been conducted, and therefore the source of ferroelectric polarization is not known. In this Rapid Communication, a neutron-diffraction measurement was performed using a single crystal to study the magnetic phase diagram.

The sample preparation procedure and the method of the electric polarization (*P*) measurement have been reported previously.[4] Magnetization (*M*) was measured with a commercial dc superconducting quantum interference magnetometer at the Center for Low Temperature Science, Tohoku University, Japan. The neutron-diffraction study was performed by using a triple-axis spectrometer PONTA installed at beam port 5G at JRR-3, JAERI, Tokai, Japan. A pyrolytic graphite monochromator was used to obtain a neutron beam with a kinetic energy of 76.3 meV. The collimations of the incident and scattered neutron beams were 40 min. The sample was mounted with its *b* axis perpendicular to the scattering plane in a closed-cycle ^{4}He refrigerator. An external magnetic field was applied parallel to the *b* axis with a split electromagnet.

Figure 1(c) shows the *M* curve at 10 K. In the initial magnetization process after the sample has been cooled to 10 K in the absence of magnetic field, *M* increases rapidly from 0.1 T and reaches saturation at $H=0.4$ T. During the process of decreasing the magnetic field, discontinuous changes are observed at $H=0.02$, 0, and −0.14 T, indicating a multistaged hysteresis, which is different from typical ferromagnetic materials. As shown in Fig. 1(d), the material exhibits a *P* of 25 $\mu C/m^2$ in a zero magnetic field. When the applied magnetic field is increased and reaches 0.13 T, *P* increases rapidly to 100 $\mu C/m^2$. The increase in *P* corresponds well with the change in *M*, which should be attributed to the phase transition of the magnetic structure.

The neutron-diffraction profile was measured to study the changes in magnetic structure when a magnetic field is applied at 10 K. As shown in Fig. 1(b), a magnetic satellite reflection of $\boldsymbol{q}=(0\ 0\ 0.62)$ which corresponds to the IC screw structure is observed in zero-field cooling (ZFC) process. This is slightly greater than the 9 K data [$\boldsymbol{q}\sim(0\ 0\ 0.58)$] obtained by Momozawa *et al.*[11] At $H=0.2$ T, this satellite reflection is lost and a commensurate magnetic reflection where $\boldsymbol{q}=(0\ 0\ 3/2)$ is observed. This modulation wave number corresponds to a double superperiod magnetic structure (twofold structure) consisting of building blocks L and S. Additionally, a broad peak where $\boldsymbol{q}=(0\ 0\ 3/4)$ corresponding to a fourfold structure is also seen, indicating that a short-range four-period magnetic ordering has formed. At $H=0.5$ T, only the $\boldsymbol{q}=(0\ 0\ 3/2)$ reflection is observed. When the magnetic field is lowered, a $\boldsymbol{q}=(0\ 0\ 1/2)$ reflection corresponding to a sixfold structure is observed, with a similar profile observable down to −0.09 T. At −0.3 T, it undergoes a transition to a twofold structure. Since *P* was measured after applying a magnetic field of 7 T at 4.3 K,[4] this result indicates that a sixfold magnetic structure is obtained in the reported weak magnetic field region in the ferroelectric phase ($P\sim25$ $\mu C/cm^2$), as well as that a twofold magnetic structure is obtained in the strong magnetic field region of the ferroelectric phase ($P\sim100$ $\mu C/cm^2$). It can be concluded that the rapid change in *P* is caused by a magnetic phase transition between these phases. Although remanent twofold magnetic region in the weak-field ferroelectric phase is suggested by small $\boldsymbol{q}=(0\ 0\ 3/2)$ reflection, the value of *P* cannot be explained by only the remanent region because a volume fraction of the region estimated from the reflection intensities is 11%. Thus we can conclude that the sixfold structure also induces the ferroelectricity.

In addition, the reflection intensity at $q=0$ also fluctuates considerably together with the magnetic modulation wave number. Figure 1(e) shows the changes in the magnetic field of the neutron reflection intensity at (1 0 −4) at 10 K. If the magnitude of the effective magnetic moments in each of the blocks L and S is uniform and the spin is collinear, the magnetic reflection intensity should be proportionate to the square of the *M*. Indeed, since the nuclear Bragg reflection is small, the dependence of this reflection intensity on the magnetic field largely agrees with the square of the *M*. If, as proposed,[5] the ferromagnetic component rotates from direction *c* to direction *b* as a result of applying a magnetic field along the *b* axis, the increase in the reflection intensity of

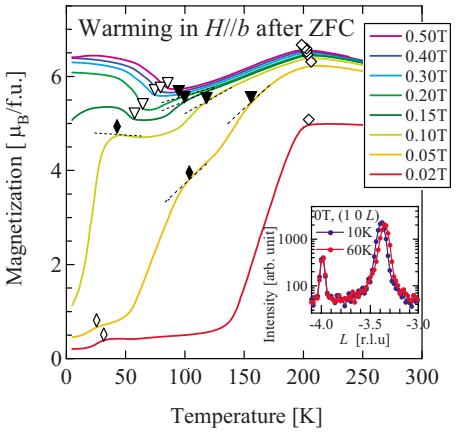

FIG. 2. (Color online) Temperature dependence of magnetization in various magnetic fields at 10 K. Measurements were performed as the temperature increased in a magnetic field after ZFC. Symbols denote magnetic transition temperatures. Inset: (1 0 L) scan profiles for $H=0$ at 60 and 10K.

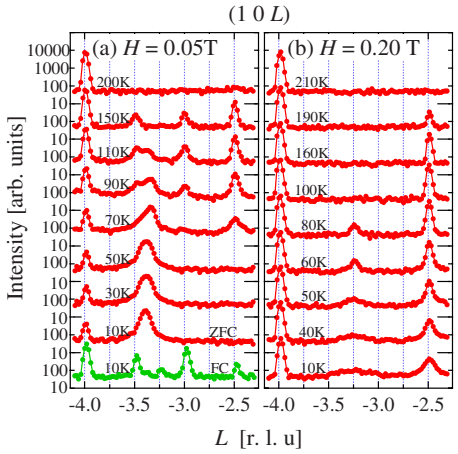

FIG. 3. (Color online) (1 0 L) scan profiles at various temperatures in a magnetic field of (a) 0.05 and (b) 0.20 T. Intensity is plotted on a logarithmic scale. In (a), data for both FC and ZFC is shown for 10 K.

(1 0 −4) is expected to be approximately 1.3-fold at most.[13] A comparison of the $H=0$ state following the ZFC process and the ferroelectric state in which the magnetic field has been reverted to zero after applying 0.5T along the b axis indicates that the ratio of the reflection intensity at (1 0 −4) is approximately fivefold. This suggests that ferroelectricity is caused by a spin structure transition whose complexity is greater than what is currently proposed.[5]

Figure 2 shows the temperature dependence of the M at various magnetic fields. At $H=0.02$ T, a transition from a ferrimagnetic structure to a proper screw structure at approximately 200 K is observed, which agrees with previous reports.[4,5] The bump at 36 K corresponds to an anomaly which has been proposed as a transition from a proper screw structure to a conical screw structure.[5] Although an increase in fundamental reflection intensity due to the increase in the ferromagnetic component and a decrease in satellite reflection intensity due to the smaller spiral surface are expected, in reality, no changes in temperature are observed in the intensity of the fundamental (1 0 −4) or the magnetic satellite reflection at (1 0 −4)+$\boldsymbol{q}$, as shown in the inset of Fig. 2. At $H=0.05$, 0.1, 0.15, and 0.2 T, several other anomalies are observed in addition to those in the vicinity of 200 K, suggesting the presence of complex phase transitions. At 0.3 T, anomalies are seen at approximately 200 and 70 K, and while the transition temperature changes at 0.4 and 0.5 T, the tendencies of the changes in temperature are the same.

The position of the magnetic satellite reflection is dependent on both temperature and magnetic field. As a typical example, Fig. 3(a) shows the changes in a (1 0 L) scan profile with temperature at $H=0.05$ T. When the temperature is lowered to 10 K with ZFC and subsequently a magnetic field of 0.05 T is applied, a $\boldsymbol{q}=(0\ 0\ 0.62)$ magnetic satellite reflection is observed, as would be the case in a zero magnetic field. When the temperature is raised, a $\boldsymbol{q}=(0\ 0\ 1/2)$ magnetic reflection occurs after a state of biphasic coexistence. Unlike the ZFC process, in the FC process, a sixfold phase with $\boldsymbol{q}=(0\ 0\ 1/2)$ is observed even at 10 K. As mentioned above, at $H=0.2$ T [see Fig. 3(b)], a sharp reflection where $\boldsymbol{q}=(0\ 0\ 3/2)$ and a broad reflection where $\boldsymbol{q}=(0\ 0\ 3/4)$ suggesting short-range ordering are observed at 10 K. The peak where $\boldsymbol{q}=(0\ 0\ 3/4)$ sharpens as the temperature rises and disappears at 100 K. The reflection for $\boldsymbol{q}=(0\ 0\ 3/2)$ also disappears at 210 K. At $H=0.05$ and 0.2 T, the temperature at which the changes in magnetic structure are observed and the temperature at which M anomalies occur correspond well.

Figure 4 shows the magnetic phase diagram obtained in this study. This diagram is more complicated than that reported previously.[5,12] The IC phase disappears with field cooling or a sweeping process of the magnetic field. A sixfold phase stabilizes in a low-temperature weak magnetic field region, and a twofold (I) phase stabilizes on the side with a stronger magnetic field. In other words, the reported

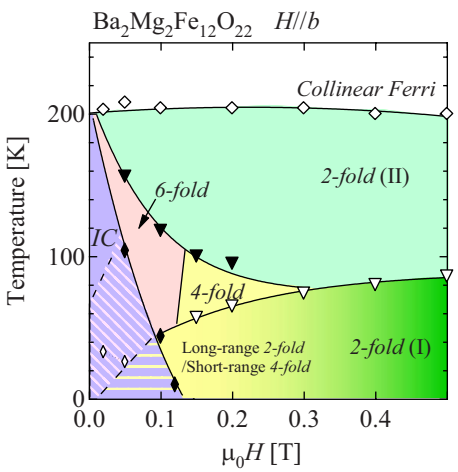

FIG. 4. (Color online) Magnetic phase diagram of $Ba_2Mg_2Fe_{12}O_{22}$. Symbols denote transition temperatures obtained from magnetization anomalies, where their shapes correspond to those shown in Fig. 2. IC denotes an incommensurate magnetic phase. Within the IC phase, diagonally and horizontally hatched regions indicate regions of the hysteresis with sixfold and twofold (I) phases, respectively.

ferroelectric phases at low temperatures[4,5] are in a sixfold phase in the weak magnetic field region and a twofold (I) phase in the strong magnetic field region. The phase transitions at low temperatures are first-order transitions accompanied by large hysteresis.

While the phase transition between the twofold (I) and the twofold (II) is clearly confirmed in a high-field region (0.3–0.5 T), where the transition temperature for several magnetic fields are denoted by the open triangles in Fig. 2, both have the same magnetic modulation wave number (0 0 3/2). In the twofold (I) phase, a four-period magnetic structure is ordered in a short range in the weak magnetic field region. While this short-range order disappears when a magnetic field is increased, it undergoes a transition to long-range order when the temperature is raised.

A comparison with the phase diagram for $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ shows that a major common point is that the incommensurate spiral magnetic structure is stabilized in a low-temperature zero magnetic field. There are two phases which have a twofold structure, where the low-temperature phase exhibits ferroelectricity. On the other hand, an obvious difference is the presence of a sixfold phase, which is observed only in $Ba_2Mg_2Fe_{12}O_{22}$. This explains why ferroelectric polarization does not occur in the weak magnetic field region for $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$.

In summary, we studied the magnetic phase diagram of a $Ba_2Mg_2Fe_{12}O_{22}$ single crystal by using neutron diffraction. The obtained phase diagram more complicated than that reported previously. We confirmed the occurrence of successive phase transitions, which are accompanied by discontinuous changes in the magnetic modulation wave number. The reported low-temperature ferroelectric phase induced by spin order were found to form a sixfold structure in weak magnetic field regions and a twofold structure in strong magnetic field regions. We have confirmed that the rapid increase in P due to the application of a magnetic field is caused by a transition between these two phases. A detailed study of magnetic structures is necessary to identify the source of electric polarization in each phase.

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[13] In reality, this ratio will be even smaller than 1.3 due to the contribution of nuclear Bragg reflection.