



Pressure-Induced Ferromagnetic to Nonmagnetic Transition and the Enhancement of Ferromagnetic Interaction in the Thiazyl-Based Organic Ferromagnet -BBDTA GaCl₄

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Pressure-induced ferromagnetic to nonmagnetic transition and the enhancement of ferromagnetic interaction in the thiazyl-based organic ferromagnet γ -BBDTA·GaCl₄

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A thiazyl-based ferromagnet, the γ -phase of BBDTA (i.e., benzo[1,2-d:4,5-d']bis[1,3,2]dithiazole)·GaCl₄, has a high ferromagnetic ordering temperature of 7.0 K in organic radical ferromagnets. In this system, pressurization generated more compact molecular packing, resulting in that the ferromagnetic state at $P = 16.2$ kbar is stabilized over a temperature range of more than twice of the initial range. However, the saturation magnetic moment was reduced with increasing pressure, decreasing to about 12 % of the initial value even at the low pressure level of $P = 1.0$ kbar. This suggests that the ferromagnetic molecular packing of the monoclinic γ -phase is easily transformed into that of the diamagnetic phase. Powder X-ray diffraction experiments revealed that the diamagnetic non-monoclinic (α - or β -) phase became stable instead of the monoclinic γ -phase across the pressure of 2.5-5.8 kbar. The increase in the temperature of onset of ferromagnetic state occurs in the surviving ferromagnetic domain surrounded by the diamagnetic domains.

KEYWORDS: Organic radical ferromagnet, Ordering temperature, Pressure effects, Structural transformation

1. Introduction

The magnetic system underlying organic radicals has attracted considerable attention from physicists and chemists with respect to its novel quantum spin system and a soft molecule-based magnet.¹⁾ The most impressive discovery in this area was the finding of a ferromagnetic order in the β -phase of *p*-NPNN (ordering temperature, $T_C = 0.60$ K) in 1991.²⁾ Subsequent studies involving the systematic synthesis of various derivatives have produced many prototype ferromagnets,¹⁻⁸⁾ which together with theoretical calculations has increased our knowledge of the potential of organic radical ferromagnets.⁹⁾ However, few high- T_C magnets with $T_C > 1.5$ K, discovered in 1993,³⁾ have been reported. Given these circumstances, cyclic thiazyl radicals have been developed to create high- T_C organic ferromagnets.^{7,8)} Rawson *et al.* have succeeded in synthesizing a ferromagnet *p*-O₂NC₆F₄CNSSN ($T_C = 1.3$ K).⁷⁾ Furthermore, Fujita and Awaga identified a ferromagnetic state with an eminently high T_C of 7.0 K in a radical cation salt, the γ -phase of BBDTA (benzo[1,2-d:4,5-d']bis[1,3,2]dithiazole)·GaCl₄ in 2004.⁸⁾ These

high T_C values in the sulfur-based system are related to strong intermolecular interactions mediated by the S \cdots S or S \cdots N interatomic contacts. Recently, some derivatives that contain heavy atoms, Se, have been found to have higher T_C in one ferromagnet ($T_C = 12.3$ K).¹⁰⁾

These studies indicate that in the near future, chemical modifications of the cyclic thiazyl radicals might allow the creation of a high- T_C ferromagnet. However, a chemical approach to molecules is not suitable for delicate manipulation of a high- T_C ferromagnet because a crystal packing of an obtained derivative is often largely different from that of an original molecule. Therefore, we have investigated physical means with applying external stress, *i.e.*, *pressure*. In contrast to inorganic materials, organic compounds are mechanically soft, so pressurization to organic materials can provide prominent changes in their intermolecular magnetic interactions even against small pressure.¹¹⁾

The present study describes the pressure-induced changes in the structure and magnetism of the cyclic thiazyl radical ferromagnet, the γ -phase of BBDTA \cdot GaCl₄. Preliminary work on the AC susceptibility has been published elsewhere.¹²⁾ The current report focuses on the detailed magnetic properties under pressure using AC and DC magnetic measurements in the pressure region up to 16.2 kbar and X-ray diffraction experiments up to 15.6 kbar.

2. Experimental Procedures

The thiazyl organic radical cation salt, BBDTA \cdot GaCl₄, has three polymorphic forms, termed α , β , and γ . The molecular structure of a BBDTA⁺ cation is shown in Fig. 1 (a). The α - and β -phases have a dimeric configuration of BBDTA cations, which confers diamagnetic properties, while BBDTA cations in the γ -phase do not form a dimeric configuration. In the γ -phase, a molecular alignment with a minimal overlapping of their molecular planes (Fig. 1(b)) results in the stabilizing of ferromagnetic ordering at 7.0 K.⁸⁾ The crystal parameters of these phases are summarized in Table I.⁸⁾ The crystals of the three phases of BBDTA \cdot GaCl₄ crystals, used in the present study, were prepared according to the procedure described elsewhere.⁸⁾

The AC susceptibility measurements were performed in an AC field with an amplitude of 2.0 Oe (peak-to-peak) and a frequency of 100 Hz, while the DC magnetization measurements in an external magnetic field (H) that ranged up to 5 T were performed using a superconducting interference device (SQUID) magnetometer (Quantum Design MPMS-5S) with an AC option. Pressure was applied using two types of piston-cylinder cell, which could be inserted into the SQUID magnetometer. The first type is a CuBe hand-made cell, in which the inner diameter for the sample space is 3.0 mm. The maximum pressure (P) for this cell was 8.45 kbar in this experiment. The second type of cell (CR-PSC-KY05-1, Kyowa-Seisakusho Co., Ltd.) has an inner diameter of 2.6 mm, and pressures of up to 16.2 kbar could be applied at the temperature of liquid helium.¹³⁾ In the latter system, the main components of the pressure cell, the cylinder, locking nuts, etc., were made of CuBe, while the pistons for transmitting the load to the sample were made of zirconia (ZrO₂). In both cells, to ensure effective application of

the pressure, the sample was held inside the Teflon cell with the aid of a pressure-transmitting medium, Apiezon-J grease, and a small amount of metallic superconducting tin or lead. The pressures applied at the temperature of liquid helium were estimated based on the shift in the superconducting transition temperature of tin¹⁴⁾ (in the first run) or lead¹⁵⁾ (in the third run). As for the second run, the pressure value was estimated from the value of the applied load,¹³⁾ because we wanted to exclude the large Meissner signal for tin or lead from the data of the M - H curve at $T = 2.0$ K.

Powder X-ray diffraction pattern analyses were carried out at pressures up to 15.6 bar at room temperature, using a synchrotron radiation X-ray powder diffractometer with a cylindrical imaging plate at the Photon Factory (PF) of the Institute of Materials Structure Science, the High Energy Accelerator Research Organization (KEK).¹⁶⁾ The wavelength of the incident X-ray was 0.6897(7) Å. Pressure was applied with a diamond-anvil cell (DAC), which consisted of diamonds with flat tips of diameter 0.6 mm and a 200- μ m-thick CuBe gasket. The pressures were calibrated by the ruby fluorescence method,¹⁷⁾ and the estimated value of pressure involves the measurement error of ± 0.8 kbar. In the sample cavity (diameter 0.2 mm), which was located in the center of the gasket, the powdered sample and a few ruby crystals were inserted with the aid of a pressure-transmitting medium, fluorine oil (FC77). When the time of braying was lengthened to reduce the crystal size, the Debye-Scherrer rings became blurred. Thus, we brayed the polycrystalline sample for only a few minutes. Consequently, the quality of the Debye-Scherrer ring was sufficiently high to perform Rietveld analyses with confidence due to the non-homogeneity of the powder size. The structure under pressure was analyzed based on the symmetry of the diffraction pattern and the peak angles.

3. Experimental Results

3.1 AC magnetic susceptibility measurements

The temperature dependence of the in-phase AC susceptibility (χ') for the γ -phase BBDTA·GaCl₄ is shown in Fig. 2, including the data for the first run ($P \leq 8.22$ kbar) (a, b), second run ($P \leq 8.45$ kbar) (c), and third run ($P \leq 16.2$ kbar) (c). Here, we defined T_C as the temperature of the magnetic anomaly, at which the extrapolating line in the region of rapid increase of (χ') crossed that in the paramagnetic region. As mentioned later, the T_C herein would not be identified with usual ferromagnetic ordering temperature under high pressure. At ambient pressure (P_0), a rapid increase in the magnitude of χ' gives the value of 7.0 K as T_C .

Under hydrostatic pressure, two independent effects were observed, (1) suppression of the magnitude of χ' and (2) enhancement of T_C . The magnitude of χ' was markedly suppressed by even a low applied pressure, and it was decreased to about a half of the initial value at a pressure of 0.10 kbar. At around 2.0 kbar of pressure, the remaining magnetic signal was 3.5 % of the original level, and this was eventually reduced to 0.07 % at 16.2 kbar.

Although the magnitude of χ' was decreased under pressure, the T_C itself increased with increasing pressure.¹²⁾ As seen in Fig. 2(c), the T_C at $P = 16.2$ kbar was >14 K. The detailed pressure dependence of T_C is shown in Fig. 3, together with previous data of magnetic ordering temperature for other organic ferromagnets, the β -phase of p -NPNN ($T_C(P_0) = 0.60$ K),^{18–20)} p -Cl-TEMPO ($T_C(P_0) = 0.28$ K),²¹⁾ 2,5-DFPNN ($T_C(P_0) = 0.45$ K),²²⁾ Dupeyredioxyl ($T_C(P_0) = 1.48$ K),²³⁾ and p -O₂NC₆F₄CN₂SSN ($T_C(P_0) = 1.30$ K).¹¹⁾ The T_C of the γ -phase BBDTA·GaCl₄ increased in a linear fashion against pressure within the studied pressure range. The gradient, dT_C/dP , was estimated to be $+5.1 \times 10^{-1}$ K/kbar, which is larger than those of other ferromagnets, as listed in Table II. As for the normalized gradient with the value of $T_C(P = 0)$, $d(T_C/T_C(P_0))/dP$, the value of $+7.3 \times 10^{-2}$ /kbar in the γ -phase BBDTA·GaCl₄ is comparable with those of other ferromagnets (see Table II). Given the above experimental results, we can estimate that T_C of the γ -phase BBDTA·GaCl₄ at $P = 18$ kbar would exceed 16 K, which is the ferromagnetic ordering temperature of TDAE-C₆₀.²⁴⁾ The tremendous increase in T_C indicates that remarkably compact intermolecular linkages through the S · · S and S · · N interatomic contacts can be realized under pressure conditions. If more compact molecular packing keeping the original molecular alignment of the γ -phase is realized, it will lead to the creation of a higher T_C ferromagnetic state in organic radical system.

3.2 Magnetization measurements

Figure 4 shows the pressure dependence of the magnetization curve of the γ -phase BBDTA·GaCl₄ at $T = 2.0$ K in the second run. We observed that the saturation magnetization decreased with increasing pressure. For reference, the data obtained for the sample in a gelatin capsule as a usual method, opened black circles, are compared to those in the pressure cell at $P = 0.00$ kbar, purple ones, as shown in Fig. 4. The saturation magnetization, M_s , of the sample in the pressure cell at 50 kOe was obviously less than that in the usual method. In the low-temperature measurement using the pressure cell, a slight mechanical stress due to thermal shrinkage and solidification of the pressure transmitting medium cannot be avoided. Such stimuli may give local stress and may induce a structural transformation to a diamagnetic or paramagnetic phase in small portion of the sample, as explained later. Figure 5 represents the pressure dependence of M_s for the first and second runs. The M_s underwent a large decrease at $P < 1$ kbar and, for $P > 1$ kbar, the pressure dependence was almost linear. Indeed, the pressure cell with ceramic parts is not suitable for DC measurements of small magnitude. Therefore, in the present study, the magnetization curve measurement was limited to pressures < 9 kbar. Based on the results shown in Fig. 5, the ferromagnetic phase was assumed to disappear at a pressure of approximately 20 kbar. The pressure-induced reduction of the magnetization observed in Fig. 4 was consistent with the pressure dependence of the intensity of the AC susceptibility, and the suppressed magnetic signal was not recovered after release of the pressure. These behaviors reveal that the ferromagnetic molecular alignment of

the γ -phase was transformed into a magnetically non-active form.

Furthermore, we found that the gradient of the M - H curve in the lower field region became gradual with increasing pressure. In fact, the reduction of M_s in the present material means the effective doping of nonmagnetic sites, resulting in the production of the ferromagnetic cluster with the finite size. Generally in a magnetically clustered system, the shape of the M - H curve correlates with the size of magnetic cluster, which is evaluated via the magnetic moment, $\mu = g\mu_B S$. Here, g is the Lande's g -factor, μ_B is the Bohr magneton, and S is the spin quantum number of the magnetic clusters in the material. The S -value of the present material under various pressures was estimated using the Langevin function as follows,

$$M = AN\mu[\coth(\mu H/k_B T) - k_B T/\mu H], \quad (1)$$

where A is fraction of the surviving ferromagnetic component, N is the Avogadro number, and k_B is the Boltzmann factor. Here, the g -value was fixed to be 2.0. The magnetic data at $P = 6.30$ kbar and 8.45 kbar were well reproduced by the equation (1). At $P = 8.45$ kbar, the solid curve in inset of Fig. 4 is the best fit with $A = 0.014$ and $S = 3.09$. These analytic results suggest that in this material, the ferromagnetic behavior survives as small ferromagnetic clusters above a specified pressure level.

3.3 Crystal structural analyses

The powder X-ray diffraction patterns of the γ -phase BBDTA·GaCl₄ under pressure are shown in Fig. 6, together with those for the α - and β -phases at ambient pressure. The γ -phase crystallizes in a monoclinic $C2/c$, while the crystal symmetry of the α - and β -phases is triclinic, as summarized in Table I. Thus, there were remarkable differences in the diffraction patterns between the γ -phase and the α - and β -phases. We could determine that five reflections at $2\theta = 5.35^\circ, 7.14^\circ, 7.34^\circ, 7.82^\circ$ and 8.06° were ascribed to the Miller indices (110), (111), (020), (200), and (021), respectively. In the case of the γ -phase, the diffraction angle region around $2\theta = 6.8^\circ, 8.9^\circ$ and 10.9° had no pronounced peaks, while as for the α - and β -phases, a few prominent peaks existed.

We see the change of diffraction pattern of the γ -phase under pressure. First, until 2.5 kbar, no drastic change in the pattern profile was noted. At $P = 5.8$ kbar, new peaks were observed at $2\theta = 6.92^\circ, 8.75^\circ,$ and 11.05° , marked by closed triangles in Fig. 6. As for the three new peaks, the corresponding peaks were seen in the α - and β -phases. This suggests that the γ -phase crystal cannot maintain the initial monoclinic structure under large stresses and a fraction of the γ -phase may be transformed into the triclinic structure under high pressure. The diffraction patterns above 12.3 kbar were similar to those of the α - or β -phase, suggesting that the γ -phase almost transformed in the triclinic phase.

Given that the α - and β -phases form a dimeric configuration between the neighboring

BBDTA⁺ radical cations, they must be more energetically stable than the γ -phase. Actually in BBDTA⁺ radical system, the dimeric configuration often appears in such a system as a spin-Peierls system²⁵⁾ and/or a system with the structural transition.²⁶⁾ We assume that the γ -phase can transform into the α - and/or β -phase of the triclinic structure under the influence of an external stress.

Here, we recall the structural data of the three phases in BBDTA·GaCl₄ (Table I). When one compares the unit cell volume per single molecule (V/Z) for these phases, the γ -phase has the highest value among the three phases, indicating that the γ -phase is the loosest packing among three phases. It is convincing that the γ -phase may transform to the other phase with tighter molecular packing under high pressure. For reference, the value of V/Z for the α -phase corresponds to 97.5 % of the γ -phase. Although it is not correct to estimate the structural parameters based on the assumption of monoclinic symmetry at $P \geq 5.8$ kbar, the unit cell volume estimated from the diffraction angles of originally strong anomalies is available as a reference point. Based on a series of the diffraction peaks, i.e., (110), (111), (020), (200), and (021) of the γ -phase, the unit cell volume of the surviving γ -phase at $P = 5.8$ kbar decreased to 97.2 % of the initial one, which is close to the above-mentioned value 97.5 %. Thus, we are convinced that above 5.8 kbar, the diffraction peaks due to the triclinic symmetry appears prominently. As reflected in the magnetic measurements, there was no reproducibility of the structural change after release of the pressure. The state at ambient pressure after releasing the pressure of 15.6 kbar was the triclinic type seen at $P \geq 5.8$ kbar. This analysis of structures under pressure shows that the γ -phase BBDTA·GaCl₄ does not have sufficient structural flexibility to resist the external stress.

Herein, the reason of the deviation between characteristic pressure on the magnetic behavior and that on structural transformation is briefly mentioned. First, even a slight pressure locally generates the magnetic vacancy by inducing the α - and/or β -phases type of dimeric structure, resulting in the rapid reduction of the ferromagnetic signal even against a small stress. In this sense, the influence of the present structural transformation with the nonmagnetic site doping appears remarkably in the magnetic measurement under low pressure. The power X-ray diffraction experiments indicate that the triclinic structure is stabilized over a large spatial region above 6 kbar. This characteristic pressure is an aim for the stabilization of triclinic transparent symmetry. Thus, it is understandable that the characteristic pressures in the magnetic measurement and structural analysis are not inconsistent.

4. Discussion

Usually antiferromagnets under high pressure generally induce enhancement of the magnetic ordering temperature, because the value of the overlap integral between the neighboring magnetic orbitals increases with increasing pressure, resulting in the enhancement of the absolute value of the intermolecular magnetic interactions.¹¹⁾ On the other hand, in the case of

ferromagnets, varied effects of pressure have been observed via the experiments of the β -phase p -NPNN,^{18–20)} p -Cl-TEMPO,²¹⁾ 2,5-DFPNN,²²⁾ Dupeyredioxyl,²³⁾ and p -O₂NC₆F₄CN₂SSN.¹¹⁾ Generally the ferromagnetic states have been known to become unstable under pressure, leading to transformation into the antiferromagnetic phases at pressures of 6–7 kbar. Exceptionally, for 2,5-DFPNN²²⁾ and p -O₂NC₆F₄CN₂SSN,¹¹⁾ pressure-induced enhancement of T_C is linear against pressure. The pressure effect on γ -phase BBDTA·GaCl₄ belongs to the latter rare case at a glance, and is accompanied by two contrasting phenomena, as discussed below.

It is necessary to discuss the mechanism to explain two independent effects: (1) the pressure-induced reduction of the susceptibility signal and saturation moment and (2) the enhancement of T_C . These phenomena are generally inconsistent with each other. The origins of (1) and (2) have to be considered independently. An overview is shown in Fig. 7. Regarding the origin of (1), we consider the structural transition from the ferromagnetic γ -phase to diamagnetic α - and/or β -phases, the molecular packings of which originally are tighter than that of the γ -phase. This scenario has been verified by the observed changes in the diffraction patterns.

As for (2), we assume that the pressure-induced enhancement of intermolecular interaction in the surviving γ -phase results in the enhancement of T_C . Indeed, the T_C appeared to exceed 16 K, which is the ferromagnetic ordering temperature of TDAE-C₆₀,²⁴⁾ at around 18 kbar. However, the measurements in additional pressure ranges are very difficult from the viewpoints of measurement sensitivity and the limit of pressure in the piston cylinder type of cell. In the present case of the γ -phase BBDTA·GaCl₄, the spin on the lattice is actually replaced to vacancy, and the randomly site-diluted system of the Heisenberg-type three-dimensional ferromagnet would be realized. Thus, the T_C shown in Fig. 3 may represent a magnetic blocking temperature above a specified pressure level. In the present experimental situation, the magnetic signal from the pressure cell prevents observations of the out-of-phase component of AC susceptibility for the sample measured under pressure. To date, we have not succeeded in detecting the dynamic properties of the pressurized state of the γ -phase.

5. Conclusion

The effects of pressure on the thiazyl organic ferromagnet γ -BBDTA·GaCl₄ were investigated by measuring AC magnetic susceptibility under hydrostatic pressures of up to 16.2 kbar. The temperature of magnetic anomaly suggesting the onset into the ferromagnetic state, which was enhanced by applying pressure, increased from 7.0 K at ambient pressure up to 14.5 K at 16.2 kbar. On the other hand, the real component of AC susceptibility decreased with increasing pressure; it was reduced to 3.5 % of the initial value at 2.0 kbar and to 0.07 % at 16.2 kbar. A similar effect was observed for the magnetization curve under pressure. The X-ray structural analyses revealed that the triclinic phase is stabilized under pressure, suggesting the structural transformation from the ferromagnetic/monoclinic structure to the

diamagnetic/triclinic one as the α -and/or β -phase. These effects of pressure can be explained by two factors: 1) a pressure-induced structural transformation from the ferromagnetic γ -phase to the diamagnetic α - and/or β -phases; and 2) an enhancement of intermolecular interactions in the surviving γ -phase. These pressure-induced physical phenomena might be considered as the effective doping of nonmagnetic sites, resulting in the production of the ferromagnetic cluster with the finite size. Furthermore, the present study reveals that pressurization can change overlap integrals of the magnetic orbitals and enhance the intermolecular interaction in the γ -BBDTA·GaCl₄, although it is very difficult to achieve large structural shrinkage while maintaining overlapping of the orthogonal molecule orbitals in the entire crystal.

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Fig. 1. Molecular structure of BBDTA⁺ (a) and crystal structures of the γ -phases of BBDTA·GaCl₄ (b).⁸⁾ Both the α - and β -phases exhibit face-to-face stacking, resulting in magnetic dimerization, while the γ -phase provides a molecular alignment with a minimal overlapping of their molecular plane (1(b)), results in the stabilizing of ferromagnetic ordering at 7.0 K.⁸⁾

Fig. 2. Temperature dependence of the real component of the AC magnetic susceptibility, χ' , for the γ -phase of BBDTA·GaCl₄, which was obtained over three runs, with the first run at $0.63 \leq P \leq 8.22$ kbar (a, b), the second run at $P \leq 8.45$ kbar (c), and the third run at $P \leq 16.2$ kbar (c).

Fig. 3. Pressure dependence of the temperature T_C for the γ -phase of BBDTA·GaCl₄ using the logarithmic scale. For reference, the previous results for five prototypes of organic radical ferromagnets are also plotted: the β -phase of *p*-NPNN,¹⁸⁻²⁰⁾ *p*-Cl-TEMPO,²¹⁾ 2,5-DFPNN,²²⁾ Dupeyredioxy,²³⁾ and *p*-O₂NC₆F₄CN₂SSN.¹¹⁾

Fig. 4. Magnetization curve for the γ -phase of BBDTA·GaCl₄ under various pressures. The results from the second run are shown. The results at $P = 6.30$ kbar and $P = 8.45$ kbar are reproduced along with the Langevin function of eq. (1). The details of the fitting parameters are provided in the text.

Fig. 5. Pressure dependence of the saturation moment M_s in the γ -phase of BBDTA·GaCl₄. The value is normalized with that at the initial state. The solid lines are guides for the eye.

Fig. 6. Powdered X-ray diffraction pattern of the γ -phase of BBDTA·GaCl₄ under pressure. The five reflections of the γ -phase at $2\theta = 5.35^\circ, 7.14^\circ, 7.34^\circ, 7.82^\circ$ and 8.06° were ascribed to the Miller indices (110), (111), (020), (200), and (021), respectively. For reference, the patterns of the α - and β -phases are shown together. The inverted triangles around $2\theta = 6.8^\circ, 8.9^\circ$ and 10.9° in the data of the γ -phase under pressure represent anomalies characteristic of the triclinic α - or β -phases.

Fig. 7. Hypothetical overview of the pressure-induced structural transformation of the γ -phase of BBDTA·GaCl₄. In the initial state, orthogonal molecular stacking is realized. However, the forced volume shrinkage probably brings about the structural transformation, as shown in the right panel. On the right side, the assumed state at around 8 kbar is depicted, in which the face-to-face molecular stacking is stabilized. However, the narrow region survives as the ferromagnetic cluster, which encompasses the physical property of ferromagnetism.

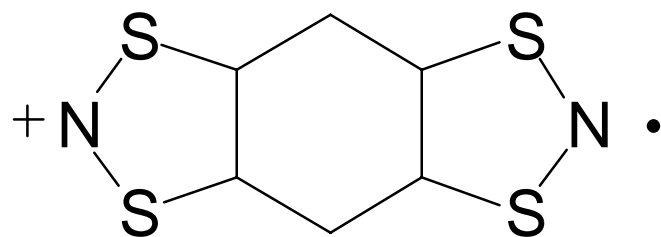
Table I. Structural symmetry, space group and lattice parameters for three phases of BBDTA·GaCl₄.⁸⁾

α -phase	β -phase	γ -phase
triclinic	triclinic	monoclinic
$P\bar{1}$	$P\bar{1}$	$C2/c$
$a = 7.904(4) \text{ \AA}$	$a = 7.272(5) \text{ \AA}$	$a = 11.260(5) \text{ \AA}$
$b = 9.681(5) \text{ \AA}$	$b = 9.734(7) \text{ \AA}$	$b = 10.851(6) \text{ \AA}$
$c = 10.918(6) \text{ \AA}$	$c = 10.423(10) \text{ \AA}$	$c = 13.209(7) \text{ \AA}$
$\alpha = 106.489(3)^\circ$	$\alpha = 111.206(3)^\circ$	
$\beta = 108.796(3)^\circ$	$\beta = 99.642(3)^\circ$	$\beta = 114.853(2)^\circ$
$\gamma = 102.458(2)^\circ$	$\gamma = 90.737(5)^\circ$	
$V = 713.67(6) \text{ \AA}^3$	$V = 675.94(9) \text{ \AA}^3$	$V = 1464.44(13) \text{ \AA}^3$
$Z = 2$	$V = 2$	$V = 4$
$V/Z = 356.84 \text{ \AA}^3$	$V = 337.97 \text{ \AA}^3$	$V = 366.11 \text{ \AA}^3$

Table II. Pressure dependence of T_C for γ -BBDTA·GaCl₄, 2,5-DFPNN²²⁾ and p -O₂NC₆F₄CN₂SSN.¹¹⁾

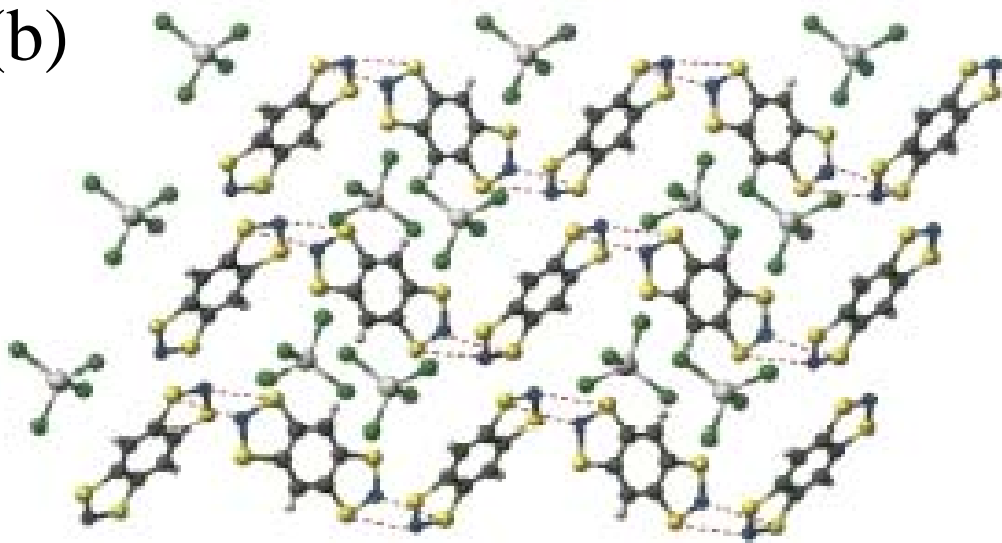
	dT_C/dP [K/kbar]	$d(T_C/T_C(P_0))/dP$ [/kbar]	$T_C(P_0)$ [K]
γ -BBDTA·GaCl ₄	$+ 5.1 \times 10^{-1}$	$+ 7.3 \times 10^{-2}$	7.0
2,5-DFPNN	$+ 7.9 \times 10^{-2}$	$+ 1.8 \times 10^{-1}$	0.45
p -O ₂ NC ₆ F ₄ CN ₂ SSN	$+ 5.9 \times 10^{-2}$	$+ 4.5 \times 10^{-2}$	1.30

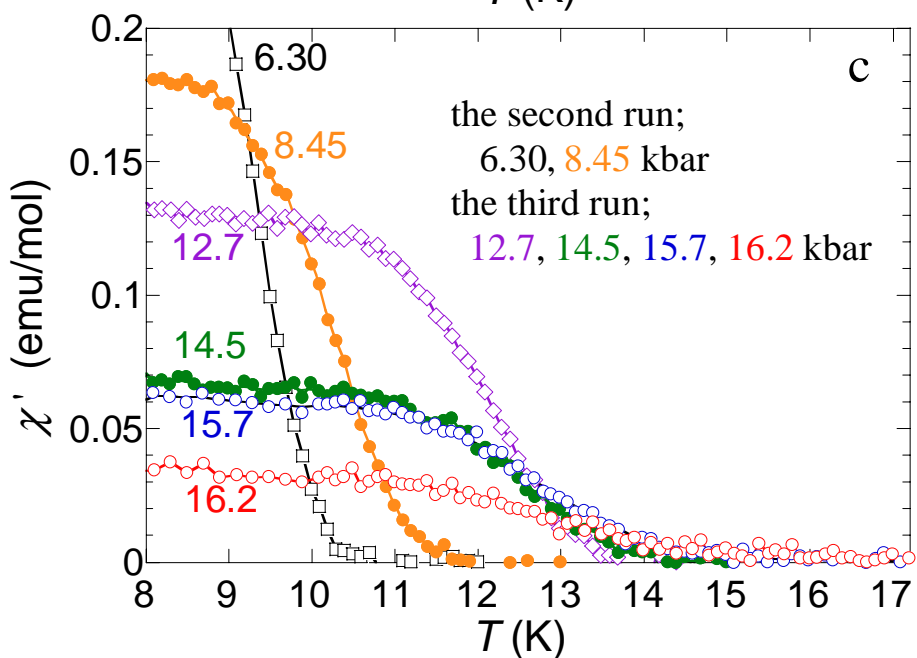
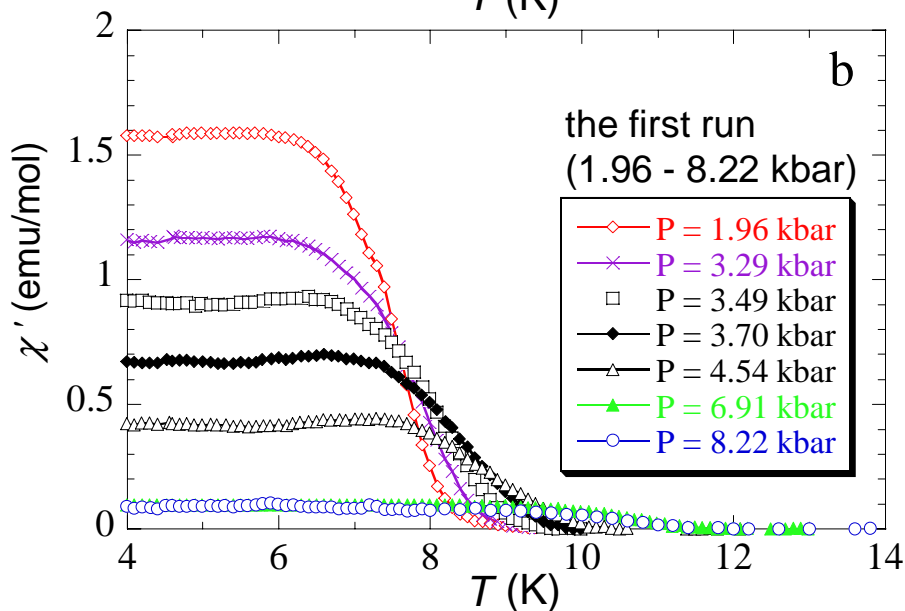
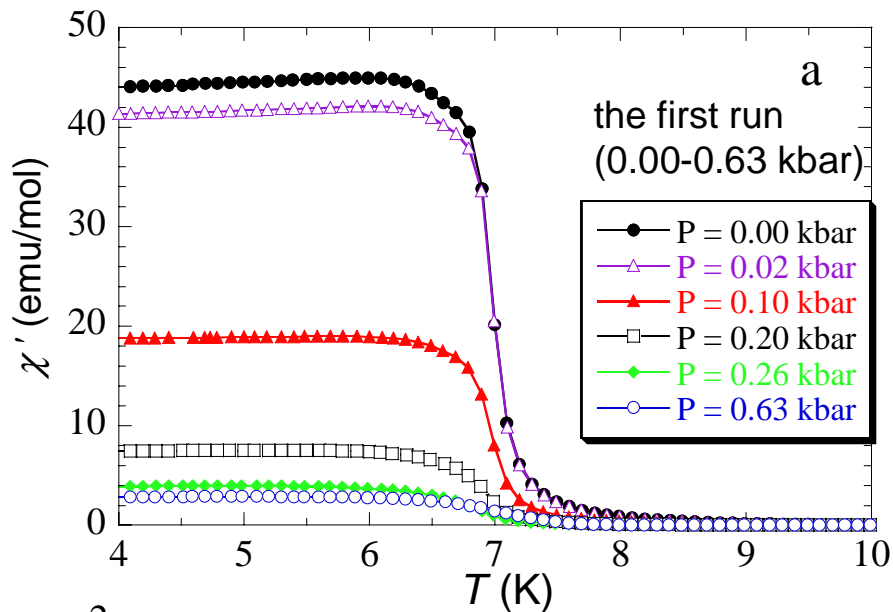
(a)

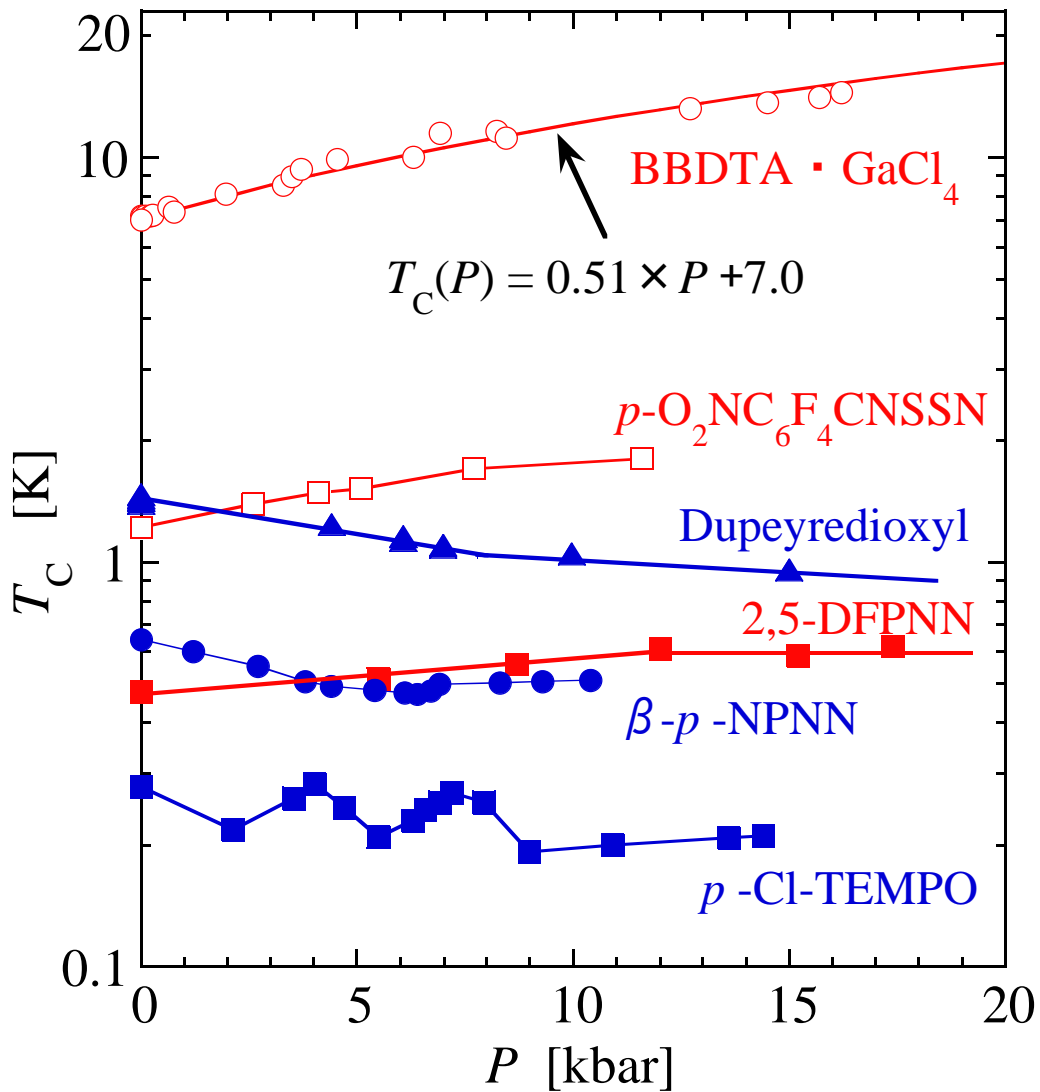


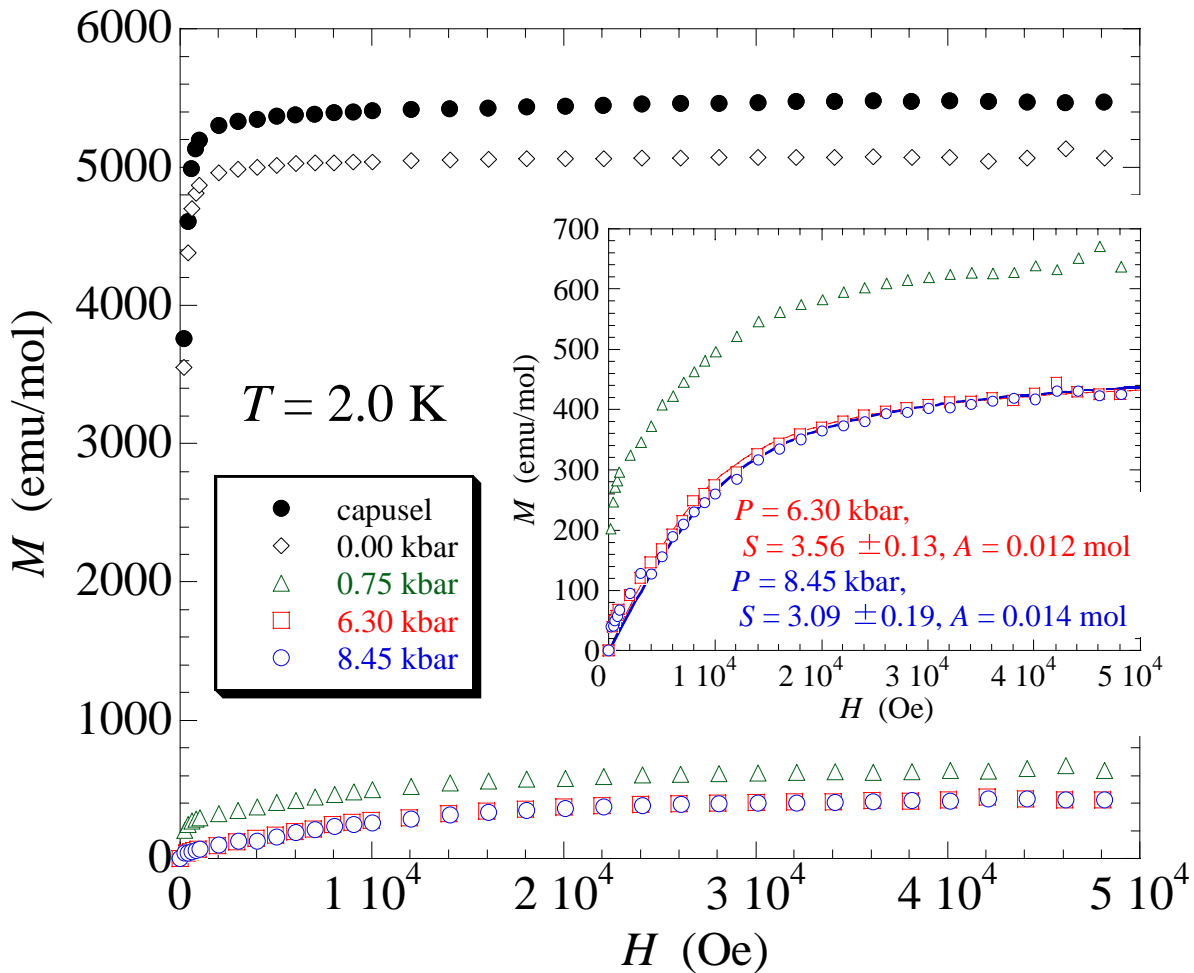
BBDTA⁺

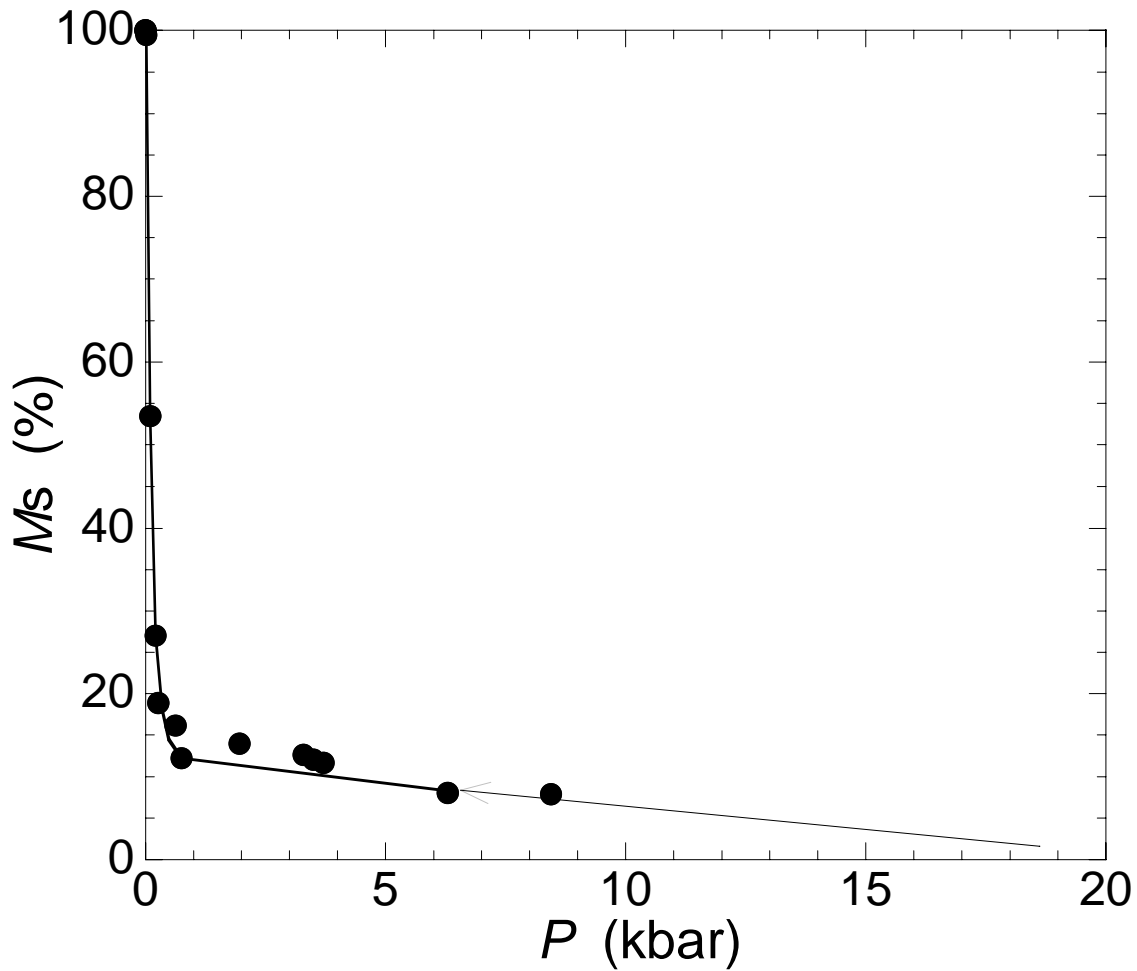
(b)

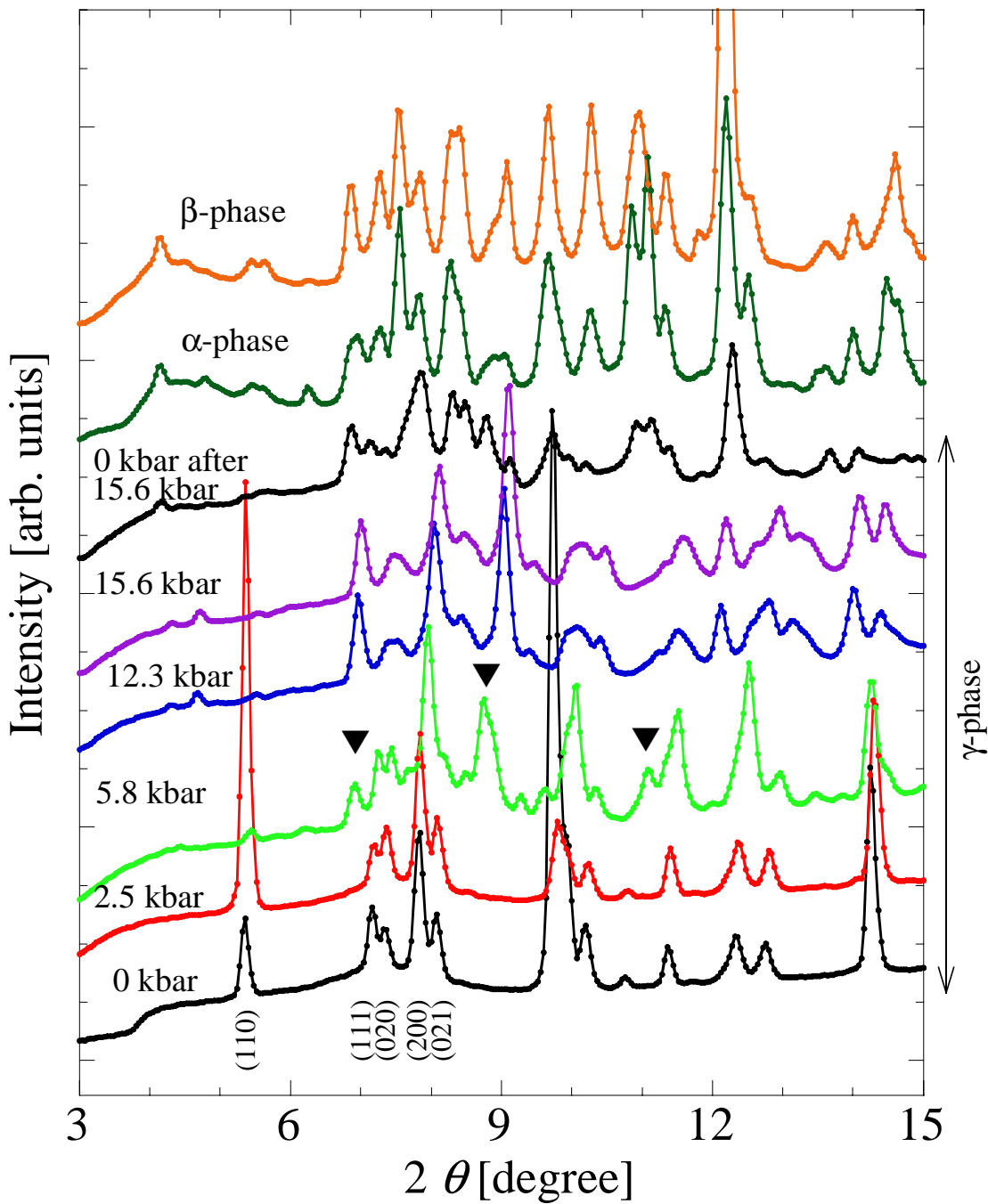




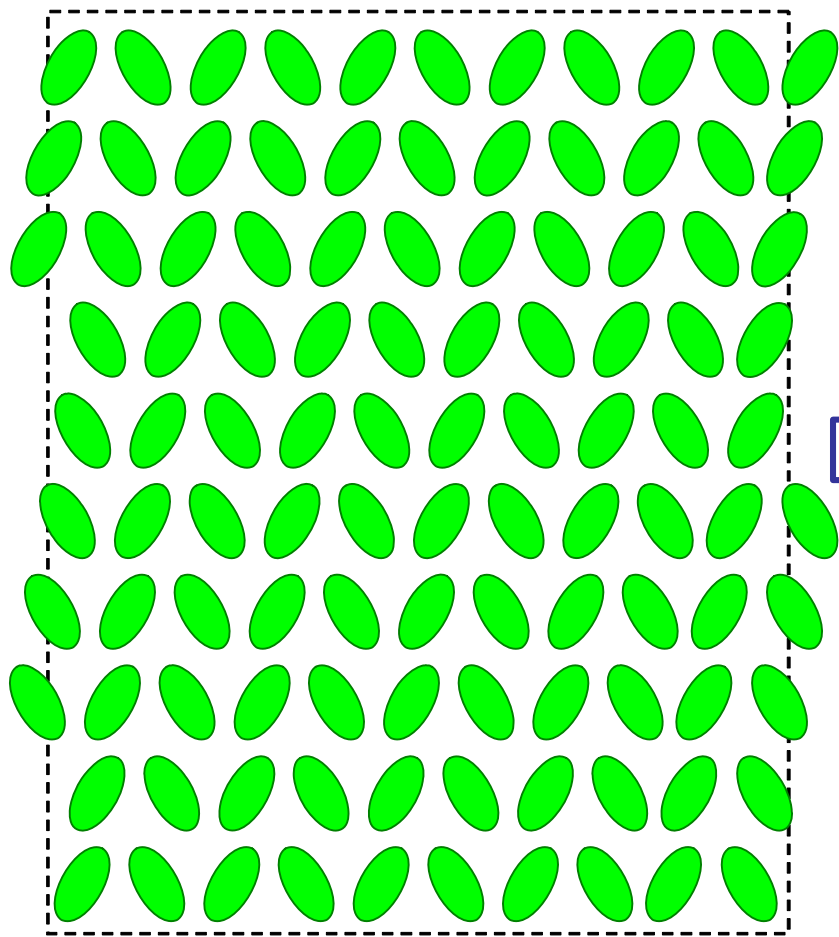




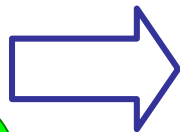




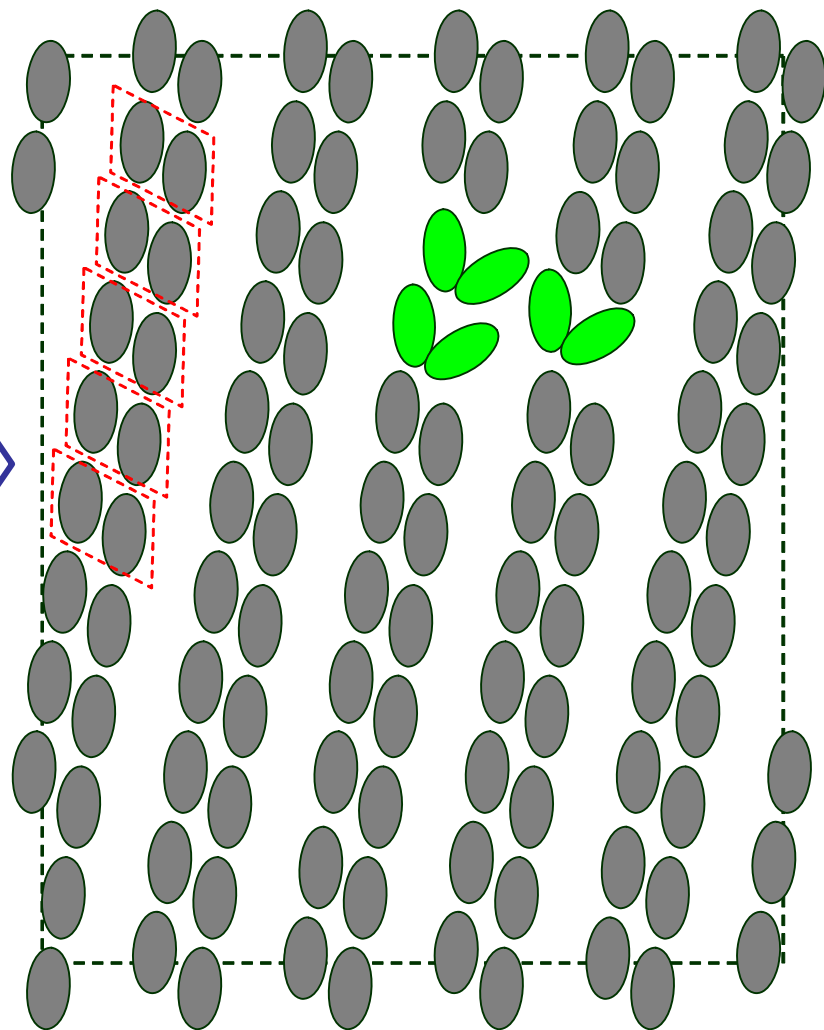
ferromagnetic phase
(γ -phase)



initial state



diamagnetic phase +
surviving ferromagnetic cluster
(γ' -phase)



stressed state ($P \sim 8\text{kbar}$)