Motivated from the flat-band ferromagnetism conceived theoretically for a single chain of five membered rings (polyaminotriazole) by Arita et al., [Phys. Rev. Lett. 88, 127202 (2002)], we have studied whether the magnetism can indeed occur as a bulk, i.e., in a three-dimensional crystal of the polymer, by means of the spin density functional calculation. We find that the intra-chain ferromagnetism is robust against crystallization as far as the flat band is made half-filled. We have further investigated the actual crystal doped with various compounds, where HF$_2$ is shown to put the system close to the bulk ferromagnetism while stronger anions such as BF$_4$ or PF$_6$ should be promising.

Materials design, especially that from the standpoint of many-body effect, is one of the most challenging avenues in condensed matter physics. In particular, designing magnets in materials consisting entirely of non-magnetic elements is an issue of great interest. In fact, a variety of ideas for exotic ferromagnetism have been proposed in this decade, where first-principles calculations are combined with electron-correlation studies for models exemplified by the Hubbard model [1–5]. In this context, organic ferromagnets are of special interest. While organic ferromagnetism has been realized in localized-spin systems such as TDAE-C$_{60}$ [6], whether we can have a band (i.e., itinerant) ferromagnetism in organics remains a challenging question.

Recently, we have proposed a new possibility of itinerant ferromagnetism in an organic polymer of five-membered rings, polyaminotriazole (PAT), and have explained the origin of the magnetism in terms of Mielke and Tasaki’s flat-band ferromagnetism [7] by coupling a first-principles band calculation with a study for the Hubbard model [4]. Concisely, the flat-band ferromagnetism occurs when there is a dispersionless band which satisfies a special condition (called connectivity condition) in the one-electron band structure. Note that the magnetism is distinct from the usual narrow-band limit in that the magnetism occurs as a quantum interference effect in the repulsively interacting system for a finite transfer energy.

While the monomer (aminotriazole) is commercially available, experimental attempts at its polymerization have just begun [8]. Experimentally, we have to aim at a bulk magnetization, so theoretically it is imperative to study whether we can have a ferromagnetism in three-dimensional crystals, which is of fundamental as well as practical interests.

The key issues are (i) the robustness of the intra-chain ferromagnetism to start with (i.e., whether the inter-chain interaction in the crystal disturbs the intra-chain ferromagnetism), (ii) whether the inter-chain interaction can be ferromagnetic (i.e., the competition between the ferromagnetic (direct-exchange) inter-chain interaction and the inter-chain energy gained by the antiferromagnetic order), and their energy scale, and (iii) which chemical dopants should be opted to bring the flat-band close to half-filling, a necessary condition for the flat-band ferromagnetism. The present paper addresses these problems.

Problem (i) is non-trivial, since the presence of adjacent chains can affect the magnetism within the chain [9]. Conversely, if the inter-chain interaction does not destroy the intra-chain ferromagnetism, this is already interesting for experimental opportunities, since if we can for example epitaxially grow the organic crystal on a metallic substrate with a large work function such as platinum, the interface state of the PAT chain can possibly have a net polarization. In fact, we shall show that the presence of neighboring chains in the crystal does not destroy the intra-chain ferromagnetism for the realistic chain-chain distance.

On the other hand, problem (ii) on the inter-chain magnetic coupling, we shall show that ferromagnetic and antiferromagnetic interactions are both small in magnitude and their competition is subtle.

As for (iii), we have studied various anions as dopants in PAT crystal to examine the magnetic property. We shall conclude that, while the dopant studied here, ClO$_4$, F, and HF$_2$, bring the system close to, but not in, the ferromagnetic phase, the chemical trend indicates that stronger anions having higher electron affinity (BF$_4$ and PF$_6$) are expected to realize the flat-band ferromagnetism.

We have adopted a first-principles band calculation within the framework of the generalized gradient approximation based on the spin-density functional theory (GGA-SDFT) to compare the total energy of vari-
ous magnetic states. In the GGA-SDFT calculations the exchange-correlation functional introduced by Perdew, Burke, and Wang [10] is adopted with the ultra-soft pseudopotential [11,12] in a separable form. The wave functions are expanded by plane waves up to a cut-off energy of 20.25 Ry.

To clarify the physics the doping has been done in two ways. We first look at the band-filling dependence by reducing the number of electrons, where a uniform negative background charge is introduced to make the system charge-neutral as in Ref. [4]. The latter part of the paper examines actual anions as dopants, where the charge transfer across the anion and PAT is calculated self-consistently.

We start with the atomic configuration of the (undoped) PAT crystal obtained by the structure-optimization, shown in Fig. 1, where the total energy is minimized with the conjugate gradient scheme [13]. We have assumed that the unit-cell is orthorhombic and contains two chains of PAT which form a herringbone structure. We have studied two types of the crystal structures, A(non-staggered) and B(staggered). Similar crystal structures have been considered in recent calculations for polythiophene [14] and poly-phenylene-vinylene [9], where PT2 and PT1 in Ref. [14] correspond to our A and B, respectively.

FIG. 1. The optimized atomic configuration of crystallized polyaminotriazole (before doping) for type A and type B. The green, white, blue balls represent C, H and N, respectively, and the square represents the unit cell.

We have determined the size of the unit-cell as follows. We first determined the dimension of the unit-cell along the chain to be 7.17 Å, which minimizes the ground state energy of an isolated chain [4]. For the unit-cell size perpendicular to the chain, we have calculated the total energies by changing the linear dimension with the increment of 1.0 au (i.e., 0.529 Å) to search for the energy minimum. The resulting unit-cell size is 8.46 Å × 6.35 Å.

We have then doped the system, first by reducing the number of electrons. We focus on the case of the half-filled flat band, for which the flat-band ferromagnetism is originally conceived. In the present crystal, top four valence bands are nearly flat to be precise (corresponding to the presence of four five-membered rings in a unit cell), and the half-filling refers to the case of one carrier per ring. We have obtained four types of solution for both A and B crystal structures in the doped case: an intra-chain ferromagnetic(F) and inter-chain antiferromagnetic(AF) state (which we call interAF hereafter), an intra-chain AF and inter-chain F state (intraAF), a state antiferromagnetic both for intra-chain and inter-chain (AF²), and finally the ferromagnetic state.

The band structure for the doped system is shown in Fig.2 for the ferromagnetic solution. For both A and B structures, we can see that the dispersion along the chain is quite similar to that of an isolated PAT chain (shown in the inset), from which we can see that the effect of the inter-chain interaction is small for the ferromagnetic state.

FIG. 2. The band structure for the ferromagnetic solution for the hole-doped crystallized polyaminotriazole in type A(a) and type B(b) structure. The black (green) lines represent the bands for the majority (minority) spin. Top-right inset shows the band structure for an isolated chain of doped polyaminotriazole.

The total energies of the three AF states for the structure A(B), as measured from those of the F state in respective structures, are, respectively: $E_{\text{interAF}} = -40 (0) \text{ meV}$, $E_{\text{intraAF}} = 130 (100) \text{ meV}$ and $E_{\text{AF}^2} = 40 (100) \text{ meV}$. If we estimate the “intra-chain magnetic coupling” as $J_{\text{intra}} = (\text{intraAF}) - E(F)$, and “inter-chain magnetic coupling” as $J_{\text{inter}} = E(\text{interAF}) - E(F)$, $J_{\text{intra}}$ is $\sim -100 \text{ meV}$ ($< 0$, i.e., ferromagnetic) for both A and B structures. If we compare this value with that for a sin-
gle PAT chain (estimated to be $\sim -50 \times 2 = -100$ meV [4], where the factor 2 is required for comparison with the present value for two chains per unit cell), the intra-chain ferromagnetism is seen to be quite robust even in the crystal.

On the other hand, the situation is subtle for $J_{\text{inter}}$. While $J_{\text{inter}}$ is estimated to be 40 meV ($> 0$, i.e., AF) for structure A, $J_{\text{inter}} \sim 0$ meV (paramagnetic) for B. This implies that F and AF interactions are both small in magnitude, so that the value of $J_{\text{inter}}$ should depend on details of the crystal structure.

![FIG. 3. (a) The optimized atomic configuration of the crystallized polyaminotriazole doped with ClO$_4$. The green, white, blue, red, pink, orange balls represent the position of the C, H, N, O, Cl and F atoms, respectively. (b) The band structure for the ferromagnetic solution. The black (green) lines represent the bands for the majority (minority) spin. (c) The wave function (sum of the squared absolute values of the top-four, majority-spin valence bands at $\Gamma$) for the ferromagnetic polyaminotriazole crystal doped with ClO$_4$. Blue (red) contours represent the amplitude around PAT (dopant).](image)

This is why we move on to first-principles calculation of the flat-band ferromagnetism for actual chemical dopants introcuded in PAT crystal. We should opt for anions having large electron affinities, because the bands of the dopants to which the charge transfer from PAT occurs will then lie well away from the bands around the Fermi energy (i.e., the flat bands). In the present study, we have studied halogens (Cl, F) and halogen compounds (ClO$_4$, HF$_2$). To make the flat bands half-filled, we put four dopants in each unit-cell that contains four five-membered rings. As for the polymorph we focus here on structure A, and we have adopted a slightly larger unit-cell size ($9.52\text{Å} \times 7.41\text{Å} \times 7.17\text{Å}$) to accommodate ClO$_4$ and HF$_2$.

We first found that we can exclude the Cl-doped case since the paramagnetic solution has a total energy lower than that for the ferromagnetic one by $\simeq 270$ meV. For ClO$_4$, F and HF$_2$, on the other hand, the ferromagnetic state becomes lower in energy than the paramagnetic state. In Fig.3(a), we show the optimized atomic configuration for the ferromagnetic solution in the ClO$_4$-doped crystal. We can see that the insertion of the ClO$_4$ molecules significantly changes the relative position of the two PAT chains in the unit-cell from those in Fig.1, which suggests that the molecules may crucially affect the electronic properties and unfavors the intra-chain ferromagnetism.

So let us turn to the band structure in Fig.3(b) to see whether the states around $E_F$ are modified. If the electron affinity of ClO$_4$ were sufficiently larger than that of PAT, the ClO$_4$-charactered bands would not hybridize with the states around $E_F$. However, the result shows that the hybridization occurs for the flat (valence-top) bands, and the Mielke-Tasaki’s orbits are severely affected.

![FIG. 4. A plot similar to Fig.3 for the fluorine-doped case.](image)

For a more quantitative argument, we have looked at the charge distribution by adopting a method due to Aizawa and Tsuneyuki [15,16] for estimating the Mulliken charge for plane-wave basis band calculations. We divide the whole system into subsystems with each subsystem containing one atom, and calculate the valence charge for each. Summing the valence charges for dopant (ClO$_4$ here), we can estimate the charge transfer from PAT to the dopant ($Q$). For PAT·ClO$_4$, we have found that $Q$ for each dopant molecule (i.e., for each five-membered ring) is $\simeq 0.88$, i.e., the charge transfer is incomplete. This suggests that the bands (Mielke-Tasaki’s) to which we wanted to hole-dope are hybridized with the dopant (ClO$_4$) band. We can indeed confirm this from the plot of the (majority-spin) wave function as a sum ($\rho$ hereafter) of the squared absolute values of flat bands at $\Gamma$ in Fig.3(c). We can see that the amplitude extends substantially to ClO$_4$, especially on O sites. In fact, the ground state becomes antiferromagnetic even within the chain, with $J_{\text{intra}} = 60$ meV and $J_{\text{inter}} = 20$ meV.
Let us now move on to the fluorine-doped case. We show the optimized atomic configuration and the band structure in Fig. 4. The band structure is similar to those plotted in Fig. 2 with the charge transfer estimated to be $Q \simeq 0.78$. The wave function in Fig. 4(c) indicates that the amplitudes on C atoms becomes considerably small, which means that the connectivity condition, necessary for the flat-band ferromagnetism [7], is violated. The exchange energies are estimated to be $J_{\text{intra}} = 40 \text{ meV}$ and $J_{\text{inter}} = 20 \text{ meV}$, so that the ground state is antiferromagnetic both within and across the chains.

Let us finally discuss the result for HF$_2$, which has the largest electron affinity among the dopants studied here. While the band structure and wave function in Fig. 5 suggest that Mielke-Tasaki’s states hybridize with anion states to some extent, the charge transfer is calculated to be $Q = 1.1$, so that this case is more promising than that of ClO$_4$ or F. While $J_{\text{intra}} \simeq 10 \text{ meV}$ and $J_{\text{intra}} \simeq 30 \text{ meV}$ are still both antiferromagnetic, $J_{\text{intra}}$ becomes considerably smaller than those for ClO$_4$ and F, reflecting the high electron affinity of HF$_2$. From the chemical trend, we may expect that a favorable situation (similar to the uniform doping described in the first half of the paper) for the ferromagnetism is expected to be realized for BF$_4$ or PF$_6$, which are known to have higher electron affinity, although a first-principles calculation for BF$_4$ or PF$_6$ would be too demanding, since these have many valence electrons or require large cut-off energies in the plane-wave expansion.

To summarize, a spin density functional calculation shows that the three-dimensional crystal of chains of five-membered rings has a robust intra-chain ferromagnetism originally conceived for an isolated polymer. For the chemical doping BF$_4$ or PF$_6$ with high electron affinity should be promising. The magnetism in the organic crystal may also be controlled by the pressure effect.

We would like to thank H. Nishihara, Y. Yamanoi and S. Nakao for fruitful discussions. This work was supported in part by a Grant-in-Aid for Creative Research (No.14Gs0297) and Special Coordination Funds for Promoting Science and Technology from Japanese Ministry of Education. The GGA calculation was performed with TAPP (Tokyo Ab-initio Program Package), where RA and YS would like to thank J. Yamauchi for useful discussions. Numerical calculations were performed on SR8000 in ISSP, University of Tokyo.

[1] N. Shima and H. Aoki, Phys. Rev. Lett. 71, 4389 (1993).
[2] S. Okada and A. Oshiyama, Phys. Rev. B 62, R13286 (1999).
[3] R. Arita, K. Kuroki, H. Aoki, A. Yajima, M. Tsukada, S. Watanabe, M. Ichimura, T. Onogi, and T. Hashizume, Phys. Rev. B 57, R6854 (1998).
[4] R. Arita, Y. Suwa, K. Kuroki, and H. Aoki, Phys. Rev. Lett. 88, 127202 (2002).
[5] K. Kusakabe and M. Maruyama, to be published in Phys. Rev. B.
[6] P.-M. Allemand, K.C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Gruner, and J.D. Thompso, Science 253, 301 (1991).
[7] For reviews, see H. Tasaki, Prog. Thoer. Phys. 99, 489 (1998); A. Mielke and H. Tasaki, Commun. Math. Phys. 158, 341 (1993).
[8] H. Nishihara and Y. Yamanoi, private communications.
[9] For a polymer, poly-phenylene-vinylene (PPV), a recent calculation [A. Ruini, M.J. Caldas, G. Bussi, and E. Molinari, Phys. Rev. Lett. 88, 206403 (2002)] has shown that the position of adjacent chains (crystalline structure) affects the state within the chain and optical properties accordingly.
[10] J.P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B 54, 16533 (1996).
[11] D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).
[12] K. Laasonen, A. Pasquarrello, R. Car, C. Lee, and D. Vanderbilt, Phys. Rev. B 47, 10142 (1993).
[13] J. Yamauchi, M. Tsukada, S. Watanabe, and O. Sugino, Phys. Rev. B 54, 5586 (1996).
[14] G. Bussi, A. Ruini, E. Molinari, M.J. Caldas, P. Puschmig, and C. Ambrosch-Draxl, Appl. Phys. Lett. 80, 4118 (2002).
[15] H. Aizawa and S. Tsumeyuki, Surf. Sci. 399, L364 (1998).
[16] Y. Suwa et al., Jpn. J. Appl. Phys. 41, 3085 (2002).