Orbital ordering and magnetic interactions in BiMnO$_3$

I V Solovyev$^{1,3}$ and Z V Pchelkina$^2$

$^1$ Computational Materials Science Center, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

$^2$ Institute of Metal Physics, Russian Academy of Sciences—Ural Division, 620041 Ekaterinburg GSP-170, Russia

E-mail: solovyev.igor@nims.go.jp

*New Journal of Physics* **10** (2008) 073021 (27pp)

Received 2 May 2008

Published 10 July 2008

Online at [http://www.njp.org/](http://www.njp.org/)

doi:10.1088/1367-2630/10/7/073021

**Abstract.** This work is devoted to the analysis of the orbital ordering patterns and associated interatomic magnetic interactions in the centrosymmetric monoclinic structures of BiMnO$_3$, which have been recently determined experimentally. First, we set up an effective lattice fermion model for the manganese 3d bands and derive parameters of this model from first-principles electronic structure calculations. Then, we solve this model in terms of the mean-field Hartree–Fock method and obtain parameters of interatomic magnetic interactions between Mn ions. We argue that although the nearest-neighbor interactions favor the ferromagnetism, they compete with the longer range antiferromagnetic (AFM) interactions, the existence of which is directly related to the peculiar geometry of the orbital ordering pattern realized in BiMnO$_3$ below 474 K. These AFM interactions favor an AFM alignment, which breaks the inversion symmetry. The formation of the AFM phase is additionally assisted by the orbital degrees of freedom, which tend to adjust the nearest-neighbor magnetic interactions in the direction which further stabilizes this phase. We propose that the multiferroelectric behavior, which was observed in BiMnO$_3$, may be related to the emergence of the AFM phase under certain conditions.

---

3 Author to whom any correspondence should be addressed.
1. Introduction

Recently, multiferroic compounds have attracted enormous attention due to their promising practical applications as well as their fundamental interest [1]–[4]. Such systems, where magnetism coexists with ferroelectricity, could be potentially used in new devices aiming to transform the information in the form of magnetization into electric voltage and back. The primary goal of theorists is to unveil the microscopic mechanism leading to the coupling between magnetic and electric degrees of freedom.

Bismuth manganite (BiMnO$_3$) has been regarded as one of the prominent multiferroic materials. Indeed, the ferromagnetism of BiMnO$_3$ is well established today. The Curie temperature ($T_C$) is about 100 K. The largest reported saturation magnetization is 3.92 $\mu_B$ per one formula unit [5], which is close to the 4 $\mu_B$ expected for the fully saturated ferromagnetic (FM) state. Nevertheless, the saturation magnetization decreases rapidly with the doping in Bi$_{1-x}$Sr$_x$MnO$_3$ [6], that may indicate the proximity of yet another, and apparently antiferromagnetic (AFM), phase.

However, the situation around the ferroelectric properties of BiMnO$_3$ is very controversial. There are several facts which support the idea that BiMnO$_3$ is not only FM, but also a ferroelectric material.

1. The existence of the ferroelectricity has been advocated by the first-principles electronic structure calculations [7], and attributed to the chemical activity of the Bi($6s^2$) lone pairs [8], in an analogy with other ferroelectric materials, such as PbTiO$_3$.

2. According to early experimental data from electron and neutron powder diffractions, BiMnO$_3$ was considered to have noncentrosymmetric $C2$ space group symmetry in the entire monoclinic region [9, 10], which is consistent with ferroelectric behavior. Namely, BiMnO$_3$ undergoes two phase transitions at the temperatures of 474 and 770 K [9, 10].

---

4 Measured at a temperature of 5 K and in a magnetic field of 5 T.
The first one, at 474 K, takes place without changing the monoclinic symmetry \([11]\). The phase transition at 770 K is monoclinic to orthorhombic \([11]\) and was believed likely to be ferroelectric–paraelectric. Nevertheless, it is worth noting that there is also another point of view according to which the onset of the ferroelectric behavior is expected only around 450 K, i.e. near the point of the isostructural monoclinic to monoclinic transition \([12]\).

3. A ferroelectric hysteresis loop has been reported both in polycrystalline and in thin film samples of BiMnO\(_3\) \([12]\), although the measured ferroelectric polarization was small (about 0.043 \(\mu\)C cm\(^{-2}\) at 200 K). For comparison, the first-principles calculations performed for the experimental noncentrosymmetric structure result in much higher polarization (about 0.52 \(\mu\)C cm\(^{-2}\)) \([13]\).

4. Kimura et al \([14]\) observed the changes of the dielectric constant induced by the magnetic field near \(T_C \sim 100\) K, and attributed them to the multiferroic behavior of BiMnO\(_3\).

5. Sharan et al \([15]\) observed electric-field-induced permanent changes in the second harmonic response from a BiMnO\(_3\) thin film, and argued that these changes are consistent with the possible presence of ferroelectricity.

However, there is also a growing evidence against the intrinsic ferroelectric behavior of BiMnO\(_3\).

1. Recently the crystal structure of BiMnO\(_3\) was re-examined by Belik et al \([5]\). After careful analysis, they concluded that both monoclinic phases observed in BiMnO\(_3\) below 770 K have centrosymmetric space group \(C2/c\). If so, BiMnO\(_3\) should be an antiferroelectric, rather than ferroelectric material. This finding was further confirmed in the neutron powder diffraction experiments by Montanari et al \([16]\) who also concluded that the crystal structure of BiMnO\(_3\) is better described by the \(C2/c\) group in a wide range of temperatures (10 \(\leq\) \(T\) \(\leq\) 295 K) and magnetic fields (0 \(\leq\) \(H\) \(\leq\) 10 T). In this respect, it is important to note that there are many objective difficulties related to the determination of the crystal structure of BiMnO\(_3\) \([17]\)^5.

2. For the similar but nonmagnetic compound BiScO\(_3\), both neutron powder and electron diffraction analyses result in the centrosymmetric \(C2/c\) space group \([19]\).

3. The structure optimization performed by using modern methods of electronic structure calculations revealed that the noncentrosymmetric \(C2\) structure, which has been reported earlier \([9, 10]\), inevitably converges to the new total energy minimum corresponding to the \(C2/c\) structure with zero net polarization \([20, 21]\).

The goal of this work is to study the orbital ordering and corresponding interatomic magnetic interactions in the centrosymmetric structure of BiMnO\(_3\). For these purposes, we construct an effective lattice fermion model and derive parameters of this model from first-principles electronic structure calculations. After solution of this model we calculate the interatomic magnetic interactions. We argue that the peculiar orbital ordering realized below 474 K gives rise to the FM interactions between the nearest neighbors, which always compete with longer range AFM interactions. We propose that the ferroelectric behavior in BiMnO\(_3\)

5 In fact, the experimental situation is complicated by samples differences (thin films or bulk), nonstoichiometry, effects of the substrate (for the thin films), etc. Some difficulties and artifacts, which may arise in experiments for multiferroic and magnetoelectric thin films, have been discussed in \([18]\).
can be related to the emergence of an AFM phase, which is stabilized by these longer range interactions and breaks the inversion symmetry.

Thus, according to our point of view, the multiferroic behavior in BiMnO$_3$ is feasible and can be associated with the competition of two magnetic phases coexisting in a narrow energy range. The centrosymmetric FM ground state itself is antiferroelectric. Nevertheless, the ferroelectricity can be observed in the noncentrosymmetric AFM phase, which can apparently exist under certain conditions. Since the ferromagnetic (antiferroelectric) and ferroelectric (antiferromagnetic) phases can be stabilized by applying, correspondingly, the magnetic and electric fields, the magnetic moment can be switched off by the electric field and vice versa. This constitutes our idea of multiferroicity in BiMnO$_3$. We rationalize several experimental facts on the basis of this picture.

The paper is organized as follows. In the next section, we discuss details of the centrosymmetric crystal structure of BiMnO$_3$. Section 3 briefly describes the results of first-principles electronic structure calculations in the local-density approximation (LDA). The construction of the model Hamiltonian is addressed in section 4. The solution of the model Hamiltonian and physical meaning of interatomic magnetic interactions is discussed in section 5. The results of calculations are considered in section 6. Finally, in section 7, we summarize our work and discuss how our results are related to the observed experimental behavior of BiMnO$_3$.

2. Crystal structure and symmetry considerations

BiMnO$_3$ has a highly distorted perovskite structure (figure 1).

In our calculations we used the experimental crystal structure for $T = 4$ and 550 K obtained by Belik et al. The experimental parameters for $T = 550$ K were taken from [5], whereas the ones for $T = 4$ K are unpublished data [22]$^6$. The primitive translations in the original monoclinic coordinate frame are given by

$$
\mathbf{a}_1 = (4.4605, -2.8019, -1.6748),
\mathbf{a}_2 = (4.4605, 2.8019, -1.6748),
\mathbf{a}_3 = (0, 0, 9.8481),
$$

(in Å, for $T = 4$ K).

The space group $C2/c$ has four symmetry operations:

$$
\hat{S}_1 = \{E|\mathbf{0}\},
\hat{S}_2 = \{I|\mathbf{0}\},
\hat{S}_3 = \{m_y|\mathbf{a}_3/2\},
\hat{S}_4 = \{C_{2y}^z|\mathbf{a}_3/2\},
$$

where in the notation $\{O|\mathbf{t}\}$, $O = E$, $I$, $m_y$, or $C_{2y}^z$ denotes the local symmetry operation, which is combined with the translation $\mathbf{t} = \mathbf{0}$ or $\mathbf{a}_3/2$. Other notations are the following: $E$ is the unity operation, $I$ is the inversion, $m_y$ is the mirror reflection of the $y$-axis, and $C_{2y}^z$ is the $180^\circ$ rotation around the $y$-axis.

$^6$ The structure parameters for $T = 4$ K are pretty close to the ones reported in [5] for $T = 300$ K. In fact, all calculations have been performed for two experimental structures corresponding to $T = 4$ and 300 K. Since the obtained results were very similar, in the following we discuss only the case of $T = 4$ K.
The primitive cell of BiMnO$_3$ has four formula units. Four Mn atoms are located at

\begin{align*}
  \text{Mn1} & : (0, -1.2069, 2.4620), \\
  \text{Mn2} & : (0, 1.2069, -2.4620), \\
  \text{Mn3} & : (2.2303, -1.4009, -0.8374), \\
  \text{Mn4} & : (2.2303, 1.4009, 4.0866),
\end{align*}

(in Å). They can be divided into two groups (Mn1, Mn2) and (Mn3, Mn4), so that in each group the atoms can be transformed to each other by the symmetry operations (1). The corresponding transformation law is given in table 1.

The FM configuration of BiMnO$_3$ has the full $C2/c$ symmetry, which excludes the ferroelectricity. Possible AFM configurations can be obtained by combining the symmetry operations (1) with the time-inversion $\hat{T}$, which flips the directions of the magnetic moments. Then, one can expect the following possibilities:

1. The AFM configuration $\uparrow\uparrow\downarrow\downarrow$ (in these notations, four arrows correspond to the directions of the magnetic moments at the Mn-sites 1, 2, 3 and 4, respectively), which transforms according to the original space group $C2/c$. Similar to the FM case, this configuration excludes the ferroelectricity.

2. The AFM configuration $\uparrow\downarrow\downarrow\uparrow$, which apart from the unity element $\{E, 0\}$, has only one symmetry operation $\hat{T} \otimes \{m_y|a_3/2\}$. This configuration does allow for the ferroelectricity,
Table 1. The transformation law of four Mn atoms in BiMnO$_3$ under symmetry operations of the $C2/c$ group. Four Mn atoms are listed in the first column. Next four columns show their images after applying the symmetry operations of the $C2/c$ group.

| Atom | $\{E\{0\}$ | $\{I\{0\}$ | $\{m_y|a_3/2\}$ | $\{C_2^\|a_3/2\}$ |
|------|-------------|-------------|----------------|----------------|
| Mn1  | Mn1         | Mn2         | Mn2            | Mn1            |
| Mn2  | Mn2         | Mn1         | Mn1            | Mn2            |
| Mn3  | Mn3         | Mn3         | Mn4            | Mn4            |
| Mn4  | Mn4         | Mn4         | Mn3            | Mn3            |

and the spontaneous polarization is expected to be perpendicular to the $y$-axis. Once the symmetry is broken by the AFM order, the atomic position will shift in order to minimize the total energy of the system via magneto-elastic interactions. In this case, the crystal symmetry is expected to be $P2$, which is compatible with the magnetic symmetry of the AFM $\uparrow\downarrow\downarrow\uparrow$ phase$^7$. Thus, the ferroelectric behavior in the $\uparrow\downarrow\downarrow\uparrow$ phase is driven by the magnetic breaking of the inversion symmetry. A similar scenario of the ferroelectric behavior has been recently considered for other manganese oxides: HoMnO$_3$ $^{23, 24}$ and TbMn$_2$O$_5$ $^{25}$.

Other combinations of $\hat{T}$ with the symmetry operations (1) will lead to unphysical solutions, where the local magnetic moments will vanish in one of the Mn-sublattices. Although such configurations are formally allowed by the symmetry, they clearly conflict with the intra-atomic Hund’s first rule and are expected to have much higher energy$^8$. We have also considered two ferrimagnetic configurations $\uparrow\downarrow\downarrow\downarrow$ and $\downarrow\downarrow\uparrow\downarrow$, which do not have any symmetry. In this case, the spontaneous polarization may have an arbitrary direction.

Below 474 K, the MnO$_6$ octahedra are strongly distorted. Around each Mn site, there are three inequivalent pairs of Mn–O bonds. At $T = 4$ K, the values of the Mn–O bondlengths are (1.899, 1.997 and 2.189 Å) and (1.930, 1.940 and 2.230 Å), around the sites Mn1 and Mn3, respectively. In the first approximation, one can say that there are four short Mn–O bonds and two long Mn–O bonds. This distortion leads to the preferential population of the $e_g$ orbitals of the $z^2$ symmetry, aligned along the long Mn–O bonds. The difference between the longest and shortest Mn–O distances around the sites Mn1 and Mn3 is 0.290 and 0.300 Å, respectively. This distortion is substantially relieved above 474 K. For example, at $T = 550$ K, the Mn–O bondlengths around the sites Mn1 and Mn3 are (2.011, 2.032 and 2.112 Å) and (1.913, 2.024 and 2.106 Å), respectively, and the difference between the longest and shortest Mn–O distances around the sites Mn1 and Mn3 is reduced to 0.101 and 0.193 Å, respectively. Thus, the reduction is the most dramatic around the site Mn1.

---

$^7$ In the other words, the distribution of the electron density in the AFM $\uparrow\downarrow\downarrow\uparrow$ phase obeys the P2 group, whereas the distribution of the magnetization density obeys the magnetic group in which $\{m_y|a_3/2\}$ is combined with $\hat{T}$.

$^8$ Note that in manganites, the intra-atomic exchange coupling $J$ is about 0.9 eV and the local magnetic moment $M$ is about 4 $\mu_B$. Therefore, the Hund energy, $-\frac{1}{4}JM^2$, is about 3.6 eV per Mn site.
Table 2. Details of LMTO calculations for BiMnO$_3$ at 4 and 550 K. The notations of the inequivalent oxygen atoms are the same as in [5].

| Type of atom | LMTO basis | Radii (Å)  |
|--------------|-------------|------------|
|              |             | 4 K    | 550 K  |
| Bi           | 6s6p6d5f    | 1.59   | 1.54   |
| Mn1          | 4s4p3d      | 1.24   | 1.32   |
| Mn3          | 4s4p3d      | 1.26   | 1.25   |
| O1           | 2s2p        | 0.98   | 1.04   |
| O2           | 2s2p        | 0.97   | 1.02   |
| O3           | 2s2p        | 0.99   | 0.97   |

3. Electronic structure in the LDA

First, we calculate the electronic structure of BiMnO$_3$ in the LDA by using the experimental information for the low- and high-temperature monoclinic structure. All calculations have been performed in the linear-muffin-tin-orbital (LMTO) method [26]–[28]. The radii of the atomic spheres and some details of the LMTO basis set used in the calculation are given in table 2. In order to better fill the unit cell volume and reduce the overlap between the atomic spheres, 36 and 42 empty spheres have been added for the 4 and 550 K structure, respectively. The resulting total and partial densities of state are shown in figure 2. The O(2p) band, lying between $-7$ and $-2$ eV, is completely filled. The electronic structure near the Fermi level is mainly formed by the Mn(3d) states. Due to the hybridization, there is also a considerable weight of the Mn(3d) states in the O(2p) band. The electronic structure near the Fermi level is further split by the pseudocubic crystal field into the Mn($e_g$) and Mn($t_{2g}$) bands, although in the highly distorted monoclinic structure there is no unique definition of the ‘$t_{2g}$’ and ‘$e_g$’ states, which are mixed by the crystal distortion. The distortion is particularly strong in the low-temperature phase, leading even to an overlap between the Mn($t_{2g}$) and Mn($e_g$) bands. The Mn($e_g$) band itself is split into the low- and high-energy subbands, lying at around 1 and 3 eV, respectively. These subbands are separated by a small gap at around 1.7 eV. In total, the low-energy Mn($e_g$) subband can accommodate four electrons (per one unit cell). Therefore, according to the formal valence argument, in the fully polarized FM phase, both Mn($t_{2g}$) and low-energy Mn($e_g$) bands are expected to be filled for the majority-spin channel, and the Fermi level is expected to fall in the gap. The crystal distortion is somewhat released in the high-temperature structure, leading to the opening of a gap between the Mn($t_{2g}$) and Mn($e_g$) bands and closing of the gap between two Mn($e_g$) subbands. The high-energy Mn($e_g$) subbands overlap with the Bi(6p) band spreading from about 2 to 5 eV.

4. Construction of the model Hamiltonian

Our next goal is the construction of an effective Hubbard-type model for the Mn(3d) bands and derivation of parameters of this model from the first-principles electronic structure calculations. The method has been proposed in [29]. Many details can be found in the review article [30].
Figure 2. Total and partial densities of states for the low-temperature (left) and high-temperature (right) monoclinic structure of BiMnO$_3$ in the LDA. The shaded area shows the contributions of the manganese 3d states. Other symbols show the positions of the main bands. The Fermi level is at zero energy.

The model itself is specified as follows:

$$\hat{H} = \sum_{\mathbf{R}\mathbf{R}'} \sum_{\alpha_1\alpha_2} t_{\mathbf{R}\mathbf{R}'}^{\alpha_1\alpha_2} \hat{c}_{\mathbf{R}\alpha_1} \hat{c}^\dagger_{\mathbf{R}'\alpha_2} + \frac{1}{2} \sum_{\mathbf{R}} \sum_{\{\alpha\}} U_{\alpha_1\alpha_2\alpha_3\alpha_4}^{\mathbf{R}} \hat{c}_{\mathbf{R}\alpha_1} \hat{c}^\dagger_{\mathbf{R}\alpha_2} \hat{c}_{\mathbf{R}'\alpha_3} \hat{c}_{\mathbf{R}'\alpha_4},$$

(2)

where $\hat{c}_{\mathbf{R}\alpha}^\dagger$ ($\hat{c}_{\mathbf{R}\alpha}$) creates (annihilates) an electron in the Wannier orbital $\tilde{W}_{\mathbf{R}\alpha}$ centered at the Mn-site $\mathbf{R}$, and $\alpha$ is a joint index, incorporating spin ($s = \uparrow$ or $\downarrow$) and orbital ($m = xy, yz, z^2, zx, x^2 - y^2$) degrees of freedom. The one-electron Hamiltonian $\hat{t}_{\mathbf{R}\mathbf{R}'} = \| t_{\mathbf{R}\mathbf{R}'}^{\alpha_1\alpha_2} \|$ usually takes into account the following contributions: the site-diagonal part ($\mathbf{R} = \mathbf{R}'$) describes the crystal-field effects, whereas the off-diagonal part ($\mathbf{R} \neq \mathbf{R}'$) stands for the transfer integrals, describing the kinetic energy of electrons.

$$U_{\alpha_1\alpha_2\alpha_3\alpha_4}^{\mathbf{R}} = \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}' \tilde{W}_{\mathbf{R}\alpha_1}^{\alpha_1\dagger}(\mathbf{r}) \tilde{W}_{\mathbf{R}'\alpha_2}^{\alpha_2\dagger}(\mathbf{r}) v_{\text{scr}}(\mathbf{r}, \mathbf{r}') \tilde{W}_{\mathbf{R}'\alpha_3}(\mathbf{r}') \tilde{W}_{\mathbf{R}\alpha_4}(\mathbf{r}')$$

are the matrix elements of the screened Coulomb interaction $v_{\text{scr}}(\mathbf{r}, \mathbf{r}')$, which are supposed to be diagonal with respect to the site indices $\{\mathbf{R}\}$. The intersite matrix elements are typically small.

Since we do not consider here the relativistic spin–orbit interaction, the matrix elements $t_{\mathbf{R}\mathbf{R}'}^{\alpha_1\alpha_2}$ are diagonal with respect to the spin indices: i.e. $t_{\mathbf{R}\mathbf{R}'}^{\alpha_1\alpha_2} = t_{\mathbf{R}\mathbf{R}'}^{m_1m_2} \delta_{s_1s_2}$. The spin dependence of the screened Coulomb interactions $U_{\alpha_1\alpha_2\alpha_3\alpha_4}^{\mathbf{R}}$ has the following form: $U_{\alpha_1\alpha_2\alpha_3\alpha_4}^{\mathbf{R}} = U_{m_1m_2m_3m_4}^{\mathbf{R}} \delta_{s_1s_2} \delta_{s_3s_4}$. Generally, the matrix elements of $\tilde{U}^{\mathbf{R}} = \| U_{\alpha_1\alpha_2\alpha_3\alpha_4}^{\mathbf{R}} \|$ depend on the site-index $\mathbf{R}$.

4.1. One-electron part

The one-electron part of the model Hamiltonian (2) can be constructed by using the formal downfolding method, which is applied to the Kohn–Sham equations in LDA. The method has been proposed in [29, 31]. It is totally equivalent to the use of the Wannier functions representation in the projector–operator method [32]. The advantage of the downfolding method...
is that by using it one can formally bypass the construction of the Wannier functions themselves and go directly to the calculation of the parameters of the model Hamiltonian. The comparison between original LDA bands and the ones obtained in the downfolding method is shown in figure 3. Generally, the agreement is nearly perfect for the low-energy Mn\textit{(t}_{2g}\textit{)} and the first four Mn\textit{(e}_{g}\textit{)} bands. In this region, the original electronic structure of the LMTO method is well reproduced after the downfolding. However, for the upper Mn\textit{(e}_{g}\textit{)} bands, which strongly overlap and interact with the Bi\textit{(6p)} bands, it is virtually impossible to reproduce all details of the electronic structure in the minimal model consisting only of the Mn\textit{(3d)} bands. Therefore, in the upper-energy region, the electronic structure obtained in the downfolding method is only an approximation to the original LDA band structure.

The model parameters for the one-electron part are obtained after the Fourier transformation of the downfolded Hamiltonian to the real space. The crystal-field splitting, obtained after the diagonalization of $\hat{t}_{RR}$, is particularly strong for the $e_{g}$ levels in the low-temperature phase, being of the order of 1.5 eV (figure 4). The origin of these crystal fields is mainly related to the change of the hybridization (or the covalent mixing) in different bonds of the distorted perovskite structure, which after the downfolding gives rise to the site-diagonal elements of the model Hamiltonian. The nonsphericity of the Madelung potential, which plays a crucial role in the $t_{2g}$ compounds [34, 35], is considerably smaller than the effects of the covalent mixing in the $e_{g}$ bands and can be neglected. The alternation of the crystal-field parameters in real space gives rise to the orbital ordering, which is primarily responsible for the magnetic behavior of BiMnO$_{3}$. This relationship will be discussed in detail in section 6.

In the high-temperature phase, the $e_{g}$-level splitting shrinks in one of the sublattices, formed by the Mn-atoms ‘1’ and ‘2’ in figure 1. In the second sublattice, formed by the Mn-atoms ‘3’ and ‘4’, the splitting is large, being of the order of 1 eV.

Because of the complexity of the transfer integrals in the monoclinic structure, it is rather difficult to monitor the behavior of individual matrix elements of $\hat{t}_{RR}$. Nevertheless, some information about the localization of $\hat{t}_{RR}$ in real space can be obtained from the analysis of

\footnote{In other words, in order to reproduce all bands we had to expand our Wannier basis and treat on an equal footing both Mn\textit{(3d)} and Bi\textit{(6p)} states.}
Figure 4. Crystal-field splitting for the low-temperature (left) and high-temperature (right) monoclinic structure of BiMnO₃. Positions of the Mn sites are shown in figure 1.

Figure 5. Distance-dependence of averaged transfer integrals, \( \bar{t}_{RR'}(d) = \left( \sum_{m_1m_2} t_{m_1m_2}^{Rm_2m_1} t_{m_2m_1}^{R'R} \right)^{1/2} \) for the low-temperature (left) and high-temperature (right) monoclinic structure of BiMnO₃. The values around two inequivalent Mn sites are shown by closed and open symbols. The positions of these Mn-sites are explained in figure 1.

Averaged parameters

\[
\bar{t}_{RR'}(d) = \left( \sum_{m_1m_2} t_{m_1m_2}^{Rm_2m_1} t_{m_2m_1}^{R'R} \right)^{1/2},
\]

where \( d \) is the distance between the Mn-sites \( R \) and \( R' \). The distance-dependence of \( \bar{t}_{RR'} \) is shown in figure 5. One can clearly see that all transfer integrals are practically restricted by the nearest neighbors at around 4 Å. The longer range interactions are considerably smaller.
4.2. Screened Coulomb interactions

The matrix elements of the screened Coulomb interactions in the Mn(3d) band, $\hat{U}_R$, can be computed in two steps [29, 30]. First, we perform the conventional constrained LDA calculations [36], and derive parameters of the on-site Coulomb interaction $u = 10 \text{ eV}$ and the intra-atomic exchange interaction $j = 1 \text{ eV}$. These parameters include several important channels of screening: for example, the screening of 3d-interactions by other electrons and the screening caused by relaxation of the atomic 3d wavefunctions are already included in the definitions of $u$ and $j$. However, there can be other contributions to the screening. Particularly, what the constrained LDA calculations typically cannot do is to treat the so-called self-screening caused by the same 3d electrons, which participate in the formation of other bands due to the hybridization effects [30]. The major contribution comes from the O(2p) band, which has a large weight of the Mn(3d) states (figure 2). This channel of screening can be included in the random-phase approximation (RPA) by starting from the interaction parameters obtained in the constrained LDA [29]:

$$\hat{U} = \left[1 - \hat{u} \hat{P}\right]^{-1} \hat{u},$$

where $\hat{P}$ is the static polarization matrix in RPA, calculated in the basis of the atomic 3d orbitals\(^{10}\), and $\hat{u}$ is the $5 \times 5 \times 5 \times 5$ matrix of the Coulomb interaction in the atomic limit. For each transition-metal site, $\hat{u}$ can be reconstructed from the parameters $u$ and $j$ by using the regular procedure, which is typically adopted in the LDA + $U$ method [30]. The polarization matrix $\hat{P}$ is computed by using the LDA band structure. Nevertheless, in order to simulate the electronic structure close to the saturated FM state, we used different Fermi levels for the majority- and minority-spin channels in the process of calculation of $\hat{P}$. Namely, it was assumed that for the minority-spin channel, the Mn(3d) band is empty and the Fermi level was placed right after the O(2p) band (i.e. around $-1.5 \text{ eV}$ in figure 3), while for the majority-spin channel, the Mn(3d) band accommodated all sixteen electrons (per one unit cell). Meanwhile, we switch off all contributions to the polarization matrix associated with the transitions between the Mn(3d) bands in order to get rid of the unphysical metallic screening, which is present in RPA if one uses the LDA band structure [37].

Then, for each Mn-site, we obtain the $5 \times 5 \times 5 \times 5$ matrix $\hat{U}_R$, which depends on $\mathbf{R}$ and incorporates some effects of the local environment. The symmetry of these matrices is also different from the spherical one. Nevertheless, just for explanatory purposes, we fit each matrix in terms of three parameters, which fully specify all intra-atomic interactions between the 3d electrons in the spherical environment: the Coulomb repulsion $U = F^0$, the intra-atomic exchange coupling $J = (F^2 + F^4)/14$, and the ‘nonsphericity’ $B = (9F^2 - 5F^4)/441$, where $F^0$, $F^2$ and $F^4$ are radial Slater’s integrals. These parameters have the following meaning: $U$ is responsible for the charge stability of certain atomic configurations, while $J$ and $B$ are responsible for the first and second Hund rule, respectively. The results of such a fitting are shown in table 3. One can clearly see that the Coulomb repulsion $U$ is greatly reduced due to the self-screening effects, while $J$ and $B$ are much closer to the atomic limit.

\(^{10}\) In the present context, the ‘atomic orbitals’ mean the muffin-tin orbitals of the LMTO method [26]–[28].
Table 3. Results of parametrization of the screened Coulomb interactions in terms of the on-site Coulomb repulsion $U$, intra-atomic exchange coupling $J$ and ‘nonsphericity’ $B$ for the low-temperature ($T = 4\, \text{K}$) and high-temperature ($T = 550\, \text{K}$) monoclinic phases of $\text{BiMnO}_3$. All parameters are measured in electron volt. Positions of the Mn-sites are shown in figure 1.

| Interaction parameters | $T = 4\, \text{K}$ | $T = 550\, \text{K}$ |
|------------------------|---------------------|----------------------|
|                        | Site 1 | Site 3 | Site 1 | Site 3 |
| $U$                    | 2.27   | 2.27   | 2.31   | 2.22   |
| $J$                    | 0.89   | 0.88   | 0.89   | 0.88   |
| $B$                    | 0.09   | 0.09   | 0.09   | 0.09   |

5. Analysis of the model Hamiltonian

5.1. Hartree–Fock approximation

In order to solve the model Hamiltonian (2), we employ the simplest mean-field Hartree–Fock approximation, where the trial many-electron wavefunction is searched for in the form of a single Slater determinant $|S[\varphi_k^s]\rangle$ constructed from the one-electron orbitals $\{\varphi_k^s\}$. In this notation, $k$ is a collective index combining the momentum $k$ in the first Brillouin zone and the band number, and $s$ is the spin of the particle. The one-electron orbitals are requested to minimize the total energy

$$E_{\text{HF}} = \min_{\{\varphi_k^s\}} \langle S[\varphi_k^s]|\hat{H}|S[\varphi_k^s]\rangle$$

for a given number of particles $N$. The minimization is equivalent to the solution of Hartree–Fock equations for $\{\varphi_k^s\}$:

$$\left(\hat{t}_k + \hat{V}^s\right) |\varphi_k^s\rangle = \epsilon_k^s |\varphi_k^s\rangle,$$

where $\hat{t}_k \equiv \|t_{k m_1 m_2}^{m_3 m_4}\|$ is the one-electron part of the model Hamiltonian (2) in the reciprocal space, $t_{k m_1 m_2}^{m_3 m_4} = \sum_{R s} t_{R R}^{m_1 m_2} e^{-i k \cdot (R - R')}$, and $\hat{V}^s \equiv \|V_{R m_1 m_2}^s\|$ is the Hartree–Fock potential,

$$V_{R m_1 m_2}^s = \sum_{m_3 m_4} \left\{ U_{R m_1 m_2 m_3 m_4}^{m_3 m_4} (n_{R m_3 m_4}^s + n_{R m_3 m_4}^\dagger) - U_{R m_1 m_2 m_3 m_4}^{m_3 m_4} (n_{R m_3 m_4}^\dagger + n_{R m_3 m_4}^s) \right\},$$

(a similar equation for $V_{R m_1 m_2}^\dagger$ is obtained by interchanging $\uparrow$ and $\downarrow$). Equation (4) is solved self-consistently together with the equation

$$\hat{n}^s = \sum_{k}^{\text{occ}} |\varphi_k^s\rangle \langle \varphi_k^s|$$

for the density matrix $\hat{n}^s \equiv \|n_{R m_1 m_2}^s\|$ in the basis of Wannier functions.

After self-consistency, the total energy (3) can be computed as

$$E_{\text{HF}} = \sum_{k s}^{\text{occ}} \epsilon_k^s - \frac{1}{2} \sum_{R s} \sum_{m_1 m_2} V_{R m_1 m_2}^s n_{R m_1 m_2}^\dagger n_{R m_1 m_2}^s.$$
5.2. Magnetic interactions

By knowing \( \{ \varepsilon_k \} \) and \( \{ \phi_k \} \), one can construct the one-electron (retarded) Green function,

\[
\hat{G}^{s}_{RR'}(\omega) = \sum_k \frac{|\phi^s_k\rangle\langle\phi^s_k|}{\omega - \varepsilon^s_k + i\delta} e^{i k \cdot (R - R')},
\]

which can be used in many applications. For example, the interatomic magnetic interactions corresponding to the infinitesimal rotations of the spin magnetic moments near the equilibrium can be obtained as [38, 39]:

\[
J^{RR'} = \frac{1}{2\pi} \text{Im} \int_{-\infty}^{\varepsilon_F} d\omega \text{Tr}_L \left\{ \hat{G}^\uparrow_{RR'}(\omega) \Delta \hat{V}_R \hat{G}^\downarrow_{RR'}(\omega) \Delta \hat{V}_R \right\},
\]

(6)

where \( \Delta \hat{V}_R = \hat{V}^\uparrow_R - \hat{V}^\downarrow_R \) is the magnetic (spin) part of the Hartree–Fock potential, \( \text{Tr}_L \) denotes the trace over the orbital indices, and \( \varepsilon_F \) is the Fermi energy. According to (6), \( J^{RR'} > 0 \) \((-<0)\) means that for the given configuration, the magnetic alignment in the bond \( \langle RR' \rangle \) corresponds to the local minimum (maximum) of the total energy. However, in the following we will use more universal notation, where \( J^{RR'} > 0 \) and \( <0 \) will denote the FM and AFM coupling, respectively. This notation corresponds to the mapping of the total energy change associated with the small rotations of the magnetic moments in the Hartree–Fock method onto the Heisenberg model [38]:

\[
E_{\text{Heis}} = -\frac{1}{2} \sum_{RR'} J^{RR'} e_R \cdot e_{R'},
\]

where \( e_R \) is the direction of the spin magnetic moment at the site \( R \).

Generally, the parameters \( \{ J^{RR'} \} \) are not universal and depend on the magnetic state in which they are calculated (for example, through the change of the orbital ordering [35] or the electronic structure [40] in each magnetic state).

If we are dealing with the collinear magnetic structure, where all spins are parallel to the \( z \)-axis, i.e. \( e_R = (0, 0, 1) \) or \( (0, 0, -1) \), one can consider a small rotation of the magnetic moment at one of the sites, \( e_R = (\sin \theta_R \cos \phi_R, \sin \theta_R \sin \phi_R, \cos \theta_R) \), and calculate the second derivative of \( E_{\text{Heis}} \) with respect to \( \theta_R \):

\[
J^0_R = \sum_{R'} J^{RR'} s^{RR'},
\]

(7)

where \( s^{RR'} = 1 \) and \(-1 \) stands correspondingly for the FM and AFM configuration in the bond \( \langle RR' \rangle \). \( J^0_R \) characterizes the stability of the magnetic system with respect to the rotation of the single spin. It can also be connected with the spin stiffness and the magnetic transition temperature in the mean-field approximation [38]. If \( J^0_R > 0 \), the magnetic system is stable, while if \( J^0_R < 0 \), it is unstable.

5.3. Decomposition into ‘double exchange’ and ‘superexchange’

Many properties of perovskite manganese oxides are related to the simple fact that the exchange splitting \( \Delta \hat{V}_R \) is large, and for many applications can be treated as the largest parameter in the problem [40, 41]. This is because Mn\(^{3+} \) ions have four unpaired 3d electrons, which interact
Figure 6. Diagonal matrix elements of the exchange splitting for five d orbitals in the low-temperature monoclinic phase. The off-diagonal matrix elements are considerably smaller. The dashed–dotted line shows the averaged value of the exchange splitting (approximately 4.7 eV). The order of 3d orbitals is $xy, yz, z^2, zx$ and $x^2 - y^2$. The geometry of the monoclinic structure and the positions of the Mn-sites are explained in figure 1.

through the Hund’s rule coupling $J$. Loosely speaking, the exchange splitting between the majority and minority spin states is controlled by the parameter $U + 3J$, which is of the order of 4.9 eV (table 3), whereas the orbital polarization (or the splitting of occupied states with one particular projection of spin) is controlled by $U - J$, being ‘only’ about 1.4 eV. Therefore, as the first approximation, one can neglect the orbital dependence of $\Delta \hat{V}_R$ and replace it by some constant exchange splitting $\Delta_{ex}$: i.e.

$$\Delta \hat{V}_{Rmm'} \rightarrow \Delta_{ex} \delta_{mm'}.$$  

(8)

A typical example of the exchange splitting in the low-temperature monoclinic phase is shown in figure 6: the averaged exchange splitting $\Delta_{ex}$ is about 4.7 eV, whereas the deviations from $\Delta_{ex}$ for the particular orbitals do not exceed 1.5 eV. Of course, the approximation (8) is rather crude. Nevertheless, as we will see below, it appears to be very useful for the analysis of interatomic magnetic interactions. It also reproduces the main trends of the behavior of these interactions at least on the semi-quantitative level.

Since $\Delta_{ex}$ is large, all minority-spin states are empty (figure 7). Therefore, all poles of $\hat{G}^\uparrow_{R' R}$ are located in the unoccupied part of the spectrum and below $\varepsilon_F$ one can use the 1/$\Delta_{ex}$ expansion for $\hat{G}^\uparrow_{R' R}$ [40, 41]. Then, the first two terms in the expansion of $J_{RR'}$ will have the following from:

$$J^D_{RR'} = \frac{1}{2\pi} \text{Im} \int_{-\infty}^{\varepsilon_F} d\omega \text{Tr}_L \left\{ \hat{G}^\uparrow_{RR'}(\omega) \hat{h}_{R' R} \right\},$$

(9)

and

$$J^S_{RR'} = \frac{1}{2\pi \Delta_{ex}} \text{Im} \int_{-\infty}^{\varepsilon_F} d\omega \text{Tr}_L \left\{ \hat{G}^\uparrow_{RR'}(\omega) \left(2\omega \hat{h}_{R' R} - (\hat{h})^2_{R' R} \right) \right\},$$

(10)

where we have used the notation $\hat{h}_{R' R} = \hat{i}_{R' R} + \hat{V}^\uparrow_{R'} \delta_{R' R}$ and $(\hat{h})^2_{R' R} = \sum_{R''} \hat{h}_{R' R''} \hat{h}_{R'' R}$.

$J^D_{RR'}$ is proportional to $\{\hat{i}_{R' R}\}$ and does not depend on $\Delta_{ex}$. In an analogy with [40, 41], we will call it ‘double exchange interaction’, although, strictly speaking, it is not a regular double exchange since $\hat{G}^\uparrow_{RR'}$ also includes $\hat{V}^\uparrow_{R}$, which takes into account the effects of the orbital

New Journal of Physics 10 (2008) 073021 (http://www.njp.org/)
Figure 7. Density of states in the FM (top) and AFM ↑↓↓↑ (bottom) phases of BiMnO$_3$, as obtained in the Hartree-Fock calculations using low-temperature (left) and high-temperature (right) monoclinic structures. The Fermi level is at zero energy (shown by dashed–dotted line). Symbols show positions of the main bands.

The division of (6) into the ‘double exchange’ and ‘superexchange’ parts was first introduced in [41] for the half-metallic cubic compounds where, similar to BiMnO$_3$ (figure 7), the bandwidth $W$ is smaller than $\Delta_{\alpha}$. The idea is based on the $1/\Delta_{\alpha}$ expansion for the Green function $\hat{G}^{\uparrow\downarrow}_{R\bar{R}}$. Then, the first term, which contributes to the nearest-neighbor interactions is $\hat{t}_{R\bar{R}}/\Delta_{\alpha}^{\downarrow\downarrow}$, whereas the second term is $2\omega\hat{t}_{R\bar{R}}/\Delta_{\alpha}^{\downarrow\uparrow}$ (note that the site-diagonal terms do not contribute to $J_{RR}'$). Since $\omega \in [-W/2, \varepsilon_F]$, the second terms are smaller and the expansion is justified. After that, one should perform the integration over $\omega$ of an oscillating function containing $\hat{G}^{\uparrow\downarrow}_{R\bar{R}}$ [42, 43]. These oscillations can lead to some cancellation effects in the expressions for $J_{RR}^D$ and $J_{RR}^S$. For example, for the half-band filling one can easily recover the canonical limit where $J_{RR}^D$ vanishes, while $J_{RR}^S$ is proportional to $\text{Tr}[\hat{\mathcal{H}}_{R\bar{R}}\hat{\mathcal{H}}_{\bar{R}R}]/\Delta_{\alpha}$ [41]. However, this is simply the band-filling effect, which does not mean the breakdown of the perturbation theory expansion. The situation is somewhat complicated by the presence of the crystal fields $\hat{t}_{R\bar{R}}$ in the distorted lattice, which can couple to the transfer integrals $\hat{t}_{R\bar{R}}$ and contribute to $J_{RR}^S$ between the nearest neighbors. However, in the latter case, one can also expect a cancelation between the first and second terms in the right-hand side of (10).
\( \hat{\mathcal{G}}_{RR}^{\uparrow} \) is the Green function corresponding to this Hamiltonian:
\[
\hat{\mathcal{G}}_{RR}^{\uparrow} = \left[ \omega - \hat{\mathcal{h}} + i\delta \right]_{RR}^{-1}.
\] (11)

In the second one, in order to be consistent with the approximate expression (8) for the exchange splitting, we will neglect all effects of the orbital polarization of the electronic origin also in the definition of \( \hat{\mathcal{h}}_{RR} \) and \( \hat{\mathcal{G}}_{RR}^{\uparrow} \), and replace \( \hat{\mathcal{h}}_{RR} \) by \( \hat{\mathcal{h}}_{RR} \) (apart from the constant shift). In this case, \( \hat{\mathcal{G}}_{RR}^{\uparrow} \) is nothing but the regular Green function in LDA. Then, it should become more clear why we continue to use the term ‘double exchange’, even though our system can be insulating already in LDA, like in the case of the low-temperature phase of BiMnO\(_3\) (figure 3). It is true that the existence of the band gap is related to some parameter of the orbital polarization, \( \Delta \). In this sense it is still reasonable to consider the superexchange processes by treating all transfer integrals as a perturbation. This would correspond to the superexchange interactions of the form \( t_{\text{eff}}^2 / \Delta \), where \( t_{\text{eff}} \) is the square of an effective transfer integral between the Mn sites, which can be expressed through \( \{ \hat{t}_{RR} \} \). However, in LDA, the orbital polarization \( \Delta \) is nothing but the crystal-field splitting, which has the same origin as \( t_{\text{eff}} \) and is caused by the covalent mixing effects. Therefore, \( \Delta \) should be proportional to \( t_{\text{eff}} \), and the total ‘superexchange’ \( t_{\text{eff}}^2 / \Delta \) should be a linear function of \( t_{\text{eff}} \), similar to the regular ‘double exchange’ processes.

6. Results and discussion

The orbital ordering in the low-temperature monoclinic phase of BiMnO\(_3\) is shown in figure 8. We have tried three different methods in order to derive the distribution of the electron density around the Mn-sites.

![Figure 8](http://www.njp.org/)
In the first method, we calculate the site-diagonal elements of the density matrix in the original LMTO basis by integrating over four lowest $e_g$ bands, and plot the electron density, which corresponds to this density matrix.

2. In the second method, we plot the distribution of the electron densities corresponding to the lowest $e_g$-orbitals, which were obtained from the diagonalization of the site-diagonal part of the downfolded Hamiltonian (in other words, the $e_g$-orbitals in this case are the crystal-field orbitals).

3. In the third method, we plot the electron densities for the occupied $\uparrow$-spin $e_g$ band, which were obtained in the Hartree–Fock calculations for the FM state (figure 7).

All three methods provide a very consistent picture for the general details of the orbital ordering in the low-temperature monoclinic phase of BiMnO$_3$, which is also consistent with results of full-potential calculations by Shishidou [20].

The orbital ordering obtained for the high-temperature structure is shown in figure 9. In this case we use only the crystal-field orbitals. Then, for the sites ‘1’ and ‘2’, which are located in the least distorted environment (figure 4), the crystal-field splitting is about 0.2 eV. This corresponds to 2100 K, which largely exceeds the temperature of the monoclinic-to-orthorhombic transition (being about 770 K [14]). The crystal-field splitting is considerably larger for the Mn-sites ‘3’ and ‘4’, which are located in the most distorted environment. Thus, it is reasonable to expect that the orbital ordering, which is controlled by the crystal-field splitting, will sustain the temperature effects and take place in both monoclinic phases, below and above 474 K. However, as it is clearly seen from the comparison of figures 8 and 9, the character of the orbital ordering will change at the point of the phase transition. This conclusion is qualitatively consistent with results of the resonant x-ray scattering on BiMnO$_3$ [44].

Figure 9. Orbital ordering obtained for the high-temperature monoclinic structure of BiMnO$_3$. Four types of Mn atoms are indicated by the numbers.
Table 4. Total energies for several AFM configurations as obtained in the Hartree–Fock calculations for the low-temperature ($T = 4$ K) and high-temperature ($T = 550$ K) monoclinic structures of BiMnO$_3$. The energies measured in meV per one formula unit relative to the FM state.

| Configuration | $T = 4$ K | $T = 550$ K |
|---------------|-----------|-------------|
| ↑↓↓↑          | 0.5       | 9.4         |
| ↑↑↓↓          | 19.0      | 48.4        |
| ↑↓↓↓          | 3.9       | 28.4        |
| ↓↓↑↓          | 5.6       | 21.5        |

Results of the Hartree–Fock calculations for the total energies, performed for the FM and several AFM configurations, are shown in table 4. One can clearly see that for the low-temperature monoclinic structure, the FM phase appears to be nearly degenerate with the AFM ↑↓↓↑ phase, which can be obtained by flipping the directions of the magnetic moments at the Mn-sites ‘2’ and ‘3’. Perhaps, the tendencies toward the antiferromagnetism are somewhat overestimated in our model, and there are several reasons for it:

1. The calculations of the Coulomb interaction $U$ are associated with certain approximations [29, 30], and in principle, some of obtained parameters can be underestimated. Our Hartree–Fock calculations show that somewhat larger values of the parameter $U$ would indeed help to stabilize the FM phase. Nevertheless, there can be other reasons why the FM state is not the most stable one. From this point of view, we do not want to treat $U$ simply as a tunable parameter and will continue to use the values derived from the calculations.

2. Our model (2) does not explicitly include the oxygen states. This appears to be a good approximation for the titanium and vanadium perovskite oxides [35], where the transition-metal and oxygen bands are well separated. However, manganese compounds are much closer to the charge-transfer regime because of the proximity of Mn(3d) and O(2p) bands, and much stronger hybridization, which takes place between these groups of states [45]–[47]. A similar situation occurs for the Mn(3d) and Bi(6p), as it was pointed out in section 4.1. Although both O(2p) and Bi(6p) states contribute to the Wannier basis for the Mn(3d) bands, as the ‘tails’ of the Wannier functions, we do not consider here any Coulomb or exchange interactions, which can occur between these tails. Some of these interactions may be important. Particularly, the magnetic polarization of the oxygen states will additionally stabilize the FM phase [48].

Nevertheless, as we will see below, the competition between FM and AFM ↑↓↓↑ phases itself is a genuine effect, which is directly related to the type of the crystal distortion and the orbital ordering in the low-temperature monoclinic structure.

The distance-dependence of interatomic magnetic interactions calculated in the low-temperature monoclinic structure is shown in figure 10. These calculations have been performed by applying the formula (6) to the FM state. We note the following. There are two types of relatively strong FM interactions between the nearest neighbors, which operate in the bonds 1–3
Figure 10. Distance-dependence of interatomic magnetic interactions in the low-temperature monoclinic phase of BiMnO$_3$. The values around two inequivalent Mn sites are shown by closed and open symbols. Other notations indicate the bonds, which participate in the formation of the FM and ↑↓↓↑ AFM structures. Positions of the Mn sites are shown in figures 1 and 11.

and 1–3″ (see figure 11 for notations). The character of these interactions is directly related to the ‘AFM’ orbital ordering in the bonds 1–3 and 1–3″, and can be anticipated already from the analysis of the distribution of the Mn–O bondlengths in the low-temperature monoclinic phase [5]. The interaction in the third bond 1–3′, formed by the nearest neighbors, is relatively weak. This is again consistent with the geometry of the orbital ordering, corresponding to the minimal overlap between occupied and unoccupied $e_g$ orbitals. A similar situation occurs in the bond 1–4′. The most striking result of the present calculations is the existence of the relatively strong long-range AFM interaction in the bond 1–2. Since the direct transfer integrals between the sites 1 and 2 are relatively small (see figure 5 and note that the distance between the sites 1 and 2 is about 8 Å), the origin of such interactions should be beyond the direct superexchange processes. Nevertheless, the appearance of such interactions is anticipated from the geometry of the orbital ordering (see figure 11). Note that the occupied $e_g$ orbitals at the sites 1 and 2 are directed toward each other. Therefore, although the direct transfer integrals between the sites 1 and 2 are small, it is still reasonable to expect the existence of AFM interactions, which are mediated by the unoccupied $e_g$ states of the intermediate site 3″. Such a situation is somewhat similar to superexchange interactions, which operate in the charge-transfer insulators via the oxygen states [45]–[47], and the mechanism itself is sometimes called ‘super-superexchange’.

Thus, in the low-temperature monoclinic phase of BiMnO$_3$ we are always dealing with the competition between nearest-neighbor FM and longer range AFM interactions. In fact,

---

12 Since in the FM structure, the atoms 3 and 4 can be transformed to each other by the symmetry operations of the $C2/c$ group, similar interactions hold between atoms 1 and 4.

13 In the present context, the ‘AFM orbital ordering’ means nearly orthogonal orientation of the occupied $e_g$ orbitals, which maximizes the virtual hoppings of electrons in the unoccupied subspace and stabilizes the FM coupling between these sites [49].
there are several factors which can make these interactions comparable with each other. It is true that, generally, the nearest-neighbor interactions are expected to be much stronger, because all transfer integrals are basically restricted by the nearest neighbors (figure 5). However, for the nearest-neighbor interactions we are also dealing with the strong cancellation of FM ‘double exchange’ and AFM superexchange contributions (table 5). For example, this cancellation is nearly perfect for the ‘weak bonds’ 1–3′ and 1–4′. This is a general rule for perovskite manganese oxides, which explains the strong reduction of the nearest-neighbor magnetic interactions, so that they can easily become comparable with some longer-range interactions [39]–[41]. On the other hand, for the longer range AFM interaction in the bond 1–2, there is no such cancellation. The long range interactions are expected to vanish for undoped (or parent) manganites, provided that they have an undistorted cubic structure. This effect is entirely related to the symmetry of filling (or half-filling) of the majority-spin $e_g$ band and the oscillating behavior of the Green function [41]. Nevertheless, many parent manganites (like BiMnO$_3$) have a strongly distorted crystal structure. This distortion gives rise to the orbital ordering, which leads to certain asymmetry of filling of the majority-spin $e_g$-states and the appearance of the longer range interactions.

The fact that the first-order (‘double exchange’) and the second-order (‘superexchange’) contributions to the nearest-neighbor interactions become comparable in the low-temperature phase of BiMnO$_3$ can look somewhat surprising. Nevertheless, we would like to emphasize that such a situation can be related to the oscillatory behavior of the Green function and does not necessary mean the breakdown of the perturbation theory expansion [42, 43] (see also discussions in footnote 11).

Thus, since the nearest-neighbor interactions favor the ferromagnetism, while the longer range interactions favor the AFM $\uparrow\downarrow\downarrow\uparrow$ structure, one can generally expect competition...
Table 5. Magnetic interactions in FM and AFM ↑↓↓↑ phases as obtained for the low-temperature ($T = 4 \text{ K}$) and high-temperature ($T = 550 \text{ K}$) monoclinic structures. The columns ‘DE’ and ‘SE’ show results of (approximate) decomposition in the double exchange and superexchange contributions using the electronic structure obtained in the Hartree–Fock calculations for the FM state and the one in LDA (in the parenthesis). All values are in meV. Positions of the Mn sites are explained in figure 11.

| Bond | $T = 4 \text{ K}$ |           | $T = 550 \text{ K}$ |           |
|------|------------------|------------|----------------------|------------|
|      | FM               | AFM        | DE                   | SE         | FM         | DE         | SE         |
| 1–3  | 5.1              | 1.7        | 32.9 (42.0)          | −30.1 (−29.5) | 15.9       | 43.2       | −30.3      |
| 1–4  | 5.1              | 7.8        | 32.9 (42.0)          | −30.1 (−29.5) | 15.9       | 43.2       | −30.0      |
| 1–3′ | −0.4             | −1.0       | 16.5 (22.4)          | −20.4 (−21.7) | 19.2       | 40.6       | −24.0      |
| 1–4′ | −0.4             | 0.7        | 16.5 (22.4)          | −20.4 (−21.7) | 19.2       | 40.6       | −24.0      |
| 1–3″  | 6.3              | 5.1        | 28.8 (36.8)          | −26.3 (−26.0) | 18.5       | 41.7       | −26.2      |
| 2–3″  | 6.3              | 5.6        | 29.8 (36.8)          | −26.3 (−26.0) | 18.5       | 41.7       | −26.2      |
| 1–2  | −3.0             | −3.0       | −0.5 (−0.7)          | −1.4 (−1.7) | 1.0        | 1.4        | 0.2        |

between these two phases, as is clearly seen from results of the total energy calculations in table 4. Nevertheless, there is another factor which will additionally stabilize the AFM ↑↓↓↑ phase and explains why it is so close in energy to the FM one.

Note that, once the magnetic structure is fixed, the orbital ordering will tend to change its form in the direction which further lowers the total energy of the system [49]. It will also change the magnetic interactions in the system. Since in BiMnO$_3$ the form of the orbital ordering is efficiently constrained by the large crystal-field splitting, the former does not strongly depend on the magnetic state, and visually one can observe only tiny changes in the distribution of the occupied e$_g$-electron density (figure 12). Nevertheless, it is interesting to see that even these tiny changes may have a profound effect on the behavior of interatomic magnetic interactions. Indeed, in the AFM ↑↓↓↑ structure, the chain 1–3″–2 contains one AFM bond (1–3″) and one FM bond (2–3″, see figure 11). Although in the AFM structure, both interactions remain FM, there is a clear polarity of these interactions, such that the magnetic coupling in the AFM bond 1–3″ is considerably weaker than the one in the FM bond 2–3″ (table 5). An even more dramatic change occurs in the plane of the distorted perovskite structure. In the AFM structure, even visually one can see some anisotropy in the distribution of the occupied e$_g$-electron density at the site 1 (figure 12), which appears to be more contracted in the direction of the FM bond 1–4. On the other hand, this distribution is nearly isotropic in the FM phase. Thus, in the direction 1–4 of the AFM phase, the weight of the e$_g$ orbitals is additionally moved into the unoccupied part of the spectrum. Such a mechanism opens some additional possibilities for the virtual hoppings in the unoccupied part of the spectrum, which will stabilize the FM coupling. Indeed, the exchange coupling in the FM bond 1–4 is 7.8 meV, while the one in the AFM bond 1–3 is strongly reduced to 1.7 meV. Moreover, the magnetic interactions in the weak bonds 1–3′ and 1–4′ are also adjusted by the change of the orbital ordering. For example, the AFM coupling in the bond 1–3′ is enhanced, while the coupling in the FM bond 1–4′ becomes FM.

New Journal of Physics 10 (2008) 073021 (http://www.njp.org/)
Figure 12. Details of orbital ordering in the FM (left) and AFM (right) phases realized in the low-temperature monoclinic structure of BiMnO$_3$. Different magnetic sublattices are shown by different colors. The arrow shows the region where the change of the orbital cloud results in the change of the interatomic magnetic interactions.

Because of these orbital effects, both magnetic configurations appear to be locally stable. Indeed, the parameters $J_{RR'}^0$, calculated in the FM and AFM $\uparrow\downarrow\uparrow\downarrow$ phases are (7.4, 12.1) and (17.6, 8.9) meV, respectively, where the first number in the parenthesis corresponds to the Mn-site 1, while the second number—to the Mn-site 3. All parameters are positive, meaning that both configurations are stable, at least with respect to independent rotations of the magnetic moments at the sites 1 and 3.

In addition to the electronic degrees of freedom, the AFM $\uparrow\downarrow\uparrow\downarrow$ phase can be stabilized by the structural effects associated with the polar atomic displacements in the direction which further minimize the total energy of the system via magneto-elastic interactions. For example, magnetic interactions in the bonds 1–3” and 2–3” can be further adjusted by displacing the Mn-atom 3” away from the mid-point (figure 11). Although we do not consider such a mechanism here (that would require detailed structural optimization using modern full-potential methods of the electronic structure calculations), it would certainly be an interesting step to do in the future. This mechanism was considered for example in [24, 25] for other multiferroic compounds.

In the high-temperature monoclinic structure, the FM phase is clearly the most stable one (table 4). This is closely related to the fact that the FM phase is metallic (figure 7). Therefore, the double exchange interactions clearly dominate (table 5). However, this is true only in the low-temperature regime. At elevated temperatures, the structure of interatomic magnetic interactions will be largely modified by the magnetic disorder, which can also destroy the metallic character of the electronic structure$^{14}$. Thus, it is rather meaningless to discuss the properties of the high-temperature phase in the low-temperature limit. The magnetic disorder in the high-temperature phase is certainly one of the interesting problems. However, it is beyond the scope of the present work. The possible tools to address this problem are the coherent potential approximation (CPA) [50, 51] or—more generally—the dynamical mean-field theory (DMFT) [52]. Nevertheless, we would like to emphasize that since the type of the orbital ordering changes in the high-temperature structure (figure 9), the magnetic interactions between

$^{14}$ In fact, the Hartree–Fock calculations for the high-temperature monoclinic structure show that only the FM phase is metallic, whereas all considered AFM phases are insulating (figure 7).

New Journal of Physics 10 (2008) 073021 (http://www.njp.org/)
the atoms 1 and 2 are expected to be weak. Therefore, the long-range AFM interactions, which according to our point of view are indispensable for the inversion symmetry breaking and appearance of the ferroelectricity, should not play any significant role in the high-temperature monoclinic phase. Thus, the temperature of the isostructural phase transition (474 K) should be also regarded as an upper bound for the possible onset of the ferroelectricity.

Finally, we would like to make several comments concerning the robustness of our conclusions against the approximations used in the process of construction of the model Hamiltonian (2) and especially related to the treatment of the oxygen states.

1. The structure of the orbital ordering around the Mn-sites is rather insensitive to the details of the treatment of the oxygen (and all other) states (see figure 8). Therefore, in the low-temperature monoclinic phase, one can generally expect the existence of the long-range AFM interactions, associated with this type of the orbital ordering, as well as the tendencies toward inversion symmetry breaking by the magnetic degrees of freedom.

2. The magnetic polarization of the oxygen states can affect the relative stability of the FM and AFM ↑↓↓↑ phases. However, the situation is not simple. On the one hand, the Wannier functions constructed for the Mn(e_g) bands have a large weight of the O(2p) states, which contribute to the magnetic polarization at the oxygen atoms [48]. On the other hand, this effect is strongly compensated by the polarization of the O(2p) band. Thus, despite the proximity to the charge-transfer regime, many properties of manganites can be treated (at least, at the semi-quantitative level) in the minimal model, which does not explicitly contain the oxygen states [40, 41, 53]. Nevertheless, the magnetic polarization of the oxygen atoms is certainly an interesting problem, which deserves careful study in the future.

3. Since the main details of the orbital ordering are controlled by the large crystal-field splitting, they are expected to be stable against temperature effects (i.e. the magnetic disorder). The polarity of the magnetic interactions in the AFM ↑↓↓↑, which is closely related to the fact that the Coulomb interaction $U$ is not particularly large so that the superexchange processes can contribute to the orbital ordering for the given magnetic state, is expected mainly below the magnetic transition temperature.

7. Implications for the properties of BiMnO_3

Thus, we would like to propose that the multiferroic behavior in BiMnO_3 should be associated with a competition between two magnetic phases. One is the centrosymmetric (and antiferroelectric) FM phase. Another one is the AFM ↑↓↓↑ phase, which breaks the inversion symmetry and allows for spontaneous electric polarization in the direction perpendicular to the $y$-axis. The existence of both phases is directly related to the peculiar orbital ordering, which takes place below 474 K.

This means that despite the fact that BiMnO_3 is crystallized in the centrosymmetric $C2/c$ structure, there is still room for the multiferroicity, if we could engineer samples where these two phases coexist in a narrow energy range accessible for the physical changes of the electric and magnetic fields as well as the temperature $T$. Then, one could readily expect the ‘switching phenomena’. For example, by applying the magnetic field $H$ one could stabilize the FM antiferroelectric phase and switch off the net electric polarization. Conversely, one could apply the electric field $E$ and stabilize the AFM ferroelectric phase with zero net magnetization.
It is true that low-temperature ferromagnetism in pure bulk samples of BiMnO$_3$ is well established today [5]. Therefore, the symmetry is expected to be $C2/c$ and these samples are not very promising from the viewpoint of multiferroic applications. However, it is also known that BiMnO$_3$ is extremely difficult to synthesize, especially in the single crystalline form. Therefore, it is reasonable to expect that BiMnO$_3$ samples will always have some defects, and we would like to speculate that these defects may play a positive role in stabilizing some fractions of the AFM and noncentrosymmetric phase. This seems to be reasonable, because the low-temperature magnetization observed in the BiMnO$_3$ samples, which do exhibit ferroelectric behavior, was only $2.6 \mu_B$ and reached $3.1 \mu_B$ per one formula unit in the high magnetic fields [12]. These values are considerably lower than the $4 \mu_B$ expected for the single saturated FM phase, meaning that the samples were not sufficiently pure and might contain some fraction of the AFM phase. This is strongly reminiscent of the idea of clustering or macroscopic phase separation, which has been intensively discussed in other perovskite manganese oxides, in the context of the colossal magnetoresistance phenomena [53, 54].

In this respect, it is important to note that even in the high-quality samples, whose low-temperature saturation magnetization was close to $4 \mu_B$ [5], the authors of [17] and [55] by means of the atomic pair distribution function analysis on neutron powder diffraction data and the selected-area electron diffraction technique, respectively, have observed the existence of short-range ordered structures (or domains) with the broken inversion symmetry. The symmetry of these structures was either $P2$ or $P2_1$, which is consistent with the crystal symmetry of the AFM $\uparrow\downarrow\downarrow\uparrow$ phase ($P2$), that we propose. Moreover, these experimental data strongly suggest that the breaking of the inversion symmetry is mainly caused by the Mn atoms, which is again consistent with the idea of the magnetic origin of this effect. Unfortunately, the authors of [17, 55] focused only on the structural properties of BiMnO$_3$, and did not provide any information on how these structural properties can be connected with the magnetic behavior of BiMnO$_3$. From our point of view, such measurements would be very useful. For example, if the origin of the noncentrosymmetric domains was indeed magnetic, it is reasonable to expect the size and the relative weight of these domains to decrease in the magnetic field.

Another possibility of controlling the properties of BiMnO$_3$ is to use thin films. In this case, due to the lattice mismatch of the bulk BiMnO$_3$ and the substrate, the latter causes an additional strain and may strongly affect the magnetic behavior of BiMnO$_3$. This effect is well known for other (colossal magnetoresistive) manganese oxides, and can be used as an efficient tool for controlling the electronic and magnetic properties near the point of the phase transition between FM and AFM states [56, 57]. Moreover, the magnetic structure at the surface of BiMnO$_3$ may also be different from the one in the bulk. Indeed, the saturation magnetization of the BiMnO$_3$ thin films grown on the (100) SrTiO$_3$ substrate was only $2.8 \mu_B$ [58], which is considerably smaller than the bulk value. The magnetic moment increases almost linearly with increasing film thickness and reaches a nearly saturated value at around 500 Å. The use of the (110) SrTiO$_3$ substrate yields even smaller saturation moment (about $1.8 \mu_B$ [58]). Thus, all these data suggest that the magnetic ground state realized in the thin films of BiMnO$_3$ is not the pure FM one, and may contain some elements of the AFM structure. Of course, on the basis of this highly limited experimental information about the saturation magnetization it is impossible to draw the ultimate conclusion that the AFM structure is indeed the noncentrosymmetric $\uparrow\downarrow\downarrow\uparrow$ one. Nevertheless, one can speculate that the ferroelectric behavior, which is apparently seen in the BiMnO$_3$ thin films, can be again related to the deviation of the magnetic structure from the pure FM one [12, 15].

New Journal of Physics 10 (2008) 073021 (http://www.njp.org/)
Finally, although the ground state of BiMnO$_3$ is FM, some fraction of the AFM $\uparrow\downarrow\downarrow\uparrow$ phase can emerge at elevated temperatures. If at zero temperature both FM and $\uparrow\downarrow\downarrow\uparrow$ AFM states are local minima of the total energy and are connected to each other by a first-order transition, the rising of the temperature can naturally lead to the coexistence of these two states due to the configuration mixing entropy. Moreover, the appearance of the two-phase state is considerably facilitated in the presence of defects [53, 54], as is well known for other (colossal magnetoresistive) manganites [59]. This behavior implies the existence of a temperature hysteresis loop in the magnetization curve near $T_C$. A small temperature hysteresis has indeed been reported in [5], which may be related to small anomalies of dielectric constant observed in [14]. Since the existence of the long-range AFM interactions is directly associated with the peculiar orbital ordering pattern persisting up to 474 K, no ferroelectricity can be generally expected above this temperature.

In summary, we believe that further exploration of the multiferroic behavior of BiMnO$_3$ should be focused on the revealing of the AFM $\uparrow\downarrow\downarrow\uparrow$ phase. Possible multiferroic applications of BiMnO$_3$ will strongly depend on whether one can find the conditions of coexistence of the FM and AFM $\uparrow\downarrow\downarrow\uparrow$ phases in a narrow energy range accessible for switching by the electric and magnetic fields. It seems that the available experimental data do not rule out this idea. We hope that our work will stimulate theoretical and experimental activities in this direction.

Acknowledgments

We are grateful to Alexei Belik for stimulating our interest in the problems of magnetism and orbital ordering in BiMnO$_3$, numerous discussions, and providing us unpublished structure parameters at 4 K. We are also grateful to Tatsuya Shishidou for the discussion of the unpublished results of his electronic structure calculations for BiMnO$_3$. The work of IVS is partly supported by a grant-in-aid for Scientific Research in Priority Area ‘Anomalous Quantum Materials’ and grant-in-aid for Scientific Research (C) no. 20540337 from the Ministry of Education, Culture, Sport, Science and Technology of Japan. The work of ZVP is partly supported by the Dynasty Foundation, Grants of the President of Russia MK-3227.2008.2, and scientific school grant SS-1929.2008.2.

References

[1] Fiebig M 2005 J. Phys. D: Appl. Phys. 38 R123
[2] Khomskii D I 2006 J. Magn. Magn. Mater. 306 1
[3] Eerenstein W, Mathur N D and Scott J F 2006 Nature 442 759
[4] Cheong S-W and Mostovoy M 2007 Nat. Mater. 6 13
[5] Belik A A et al 2007 J. Am. Chem. Soc. 129 971
[6] Chiba H, Atou T and Syono Y 1997 J. Solid State Chem. 132 139
[7] Hill N A and Rabe K M 1999 Phys. Rev. B 59 8759
[8] Seshadri R and Hill N A 2001 Chem. Mater. 13 2892
[9] Atou T, Chiba H, Ohoyama K, Yamaguchi Y and Syono Y 1999 J. Solid State Chem. 145 639
[10] Moreira dos Santos A, Cheetham A K, Atou T, Syono Y, Yamaguchi Y, Ohoyama K, Chiba H and Rao C N R 2002 Phys. Rev. B 66 064425
[11] Montanari E, Calestani G, Migliori A, Dapiaggi M, Bolzoni F, Cabassi R and Gilioli ed 2005 Chem. Mater. 17 6457

New Journal of Physics 10 (2008) 073021 (http://www.njp.org/)
[12] Moreira dos Santos A, Parashar S, Raju A R, Znao Y S, Cheetham A K and Rao C N R 2002 *Solid State Commun.* **122** 49
[13] Shishidou T, Mikamo N, Uratani Y, Ishii F and Oguchi T 2004 *J. Phys.: Condens. Matter* **16** S5677
[14] Kimura T, Kawamoto S, Yamada I, Azuma M, Takano M and Tokura Y 2003 *Phys. Rev. B* **67** 184041
[15] Sharan A, Lettieri J, Jia Y, Tian W, Pan X, Schlom D G and Gopalan V 2004 *Phys. Rev. B* **69** 214109
[16] Montanari E, Caliestri G, Righi L, Gilioli E, Bolzoni F, Knight K S and Radaelli P G 2007 *Phys. Rev. B* **75** 220101
[17] Yokosawa T, Belik A A, Asaka T, Kimoto K, Takayama-Muromachi E and Matsui Y 2008 *Phys. Rev. B* **77** 024111
[18] Eerenstein W, Morrison F D, Sher F, Prieto J L, Attfield J P, Scott J F and Mathur N D 2007 *Phil. Mag. Lett.* **87** 249
[19] Belik A A et al 2006 *J. Am. Chem. Soc.* **128** 706
[20] Shishidou T 2007 private communication
[21] Baettig P, Seshadri R and Spaldin N A 2007 *J. Am. Chem. Soc.* **129** 9854
[22] Belik 2007 private communication
[23] Sergienko I A, Shen C and Dagotto E 2006 *Phys. Rev. Lett.* **97** 227204
[24] Piccozi S, Yamauchi K, Sanyal B, Sergienko I A and Dagotto E 2007 *Phys. Rev. Lett.* **99** 227201
[25] Wang C, Guo G-C and He L 2007 *Phys. Rev. Lett.* **99** 177202
[26] Andersen O K 1975 *Phys. Rev. B* **12** 3060
[27] Gunnarsson O, Jepsen O and Andersen O K 1983 *Phys. Rev. B* **27** 7144
[28] Andersen O K and Jepsen O 1984 *Phys. Rev. Lett.* **53** 2571
[29] Solovyev I V 2006 *Phys. Rev. B* **73** 155117
[30] Solovyev I V 2008 J. Phys.: Condens. Matter **20** 293201
[31] Solovyev I V 2004 *Phys. Rev. B* **69** 134403
[32] Solovyev I V, Pchelkina Z V and Anisimov V I 2007 *Phys. Rev. B* **75** 045110
[33] Bradley C J and Cracknell A P 1972 *The Mathematical Theory of Symmetry in Solids* (Oxford: Clarendon)
[34] Mochizuki M and Imada M 2003 *Phys. Rev. Lett.* **91** 167203
[35] Solovyev I V 2006 *Phys. Rev. B* **74** 054412
[36] Gunnarsson O, Andersen O K, Jepsen O and Zaanen J 1989 *Phys. Rev. B* **39** 1708
[37] Aryasetiawan F, Imada M, Georges A, Kotliar G, Biermann S and Lichtenstein A I 2004 *Phys. Rev. B* **70** 195104
[38] Liechtenstein A I, Katsnelson M I, Antropov V P and Gubanov V A 1987 *J. Magn. Magn. Mater.* **67** 65
[39] Solovyev I V 2003 Magnetic interactions in transition-metal oxides Recent Research Developments in *Magnetism and Magnetic Materials* vol 1 (India: Transworld Research Network) p 253
[40] Solovyev I V and Terakura K 2003 Orbital degeneracy and magnetism of perovskite manganese oxides *Electronic Structure and Magnetism of Complex Materials* ed D J Singh and D A Papaconstantopoulos (Berlin: Springer) p 253
[41] Solovyev I V and Terakura K 1999 *Phys. Rev. Lett.* **82** 2959
[42] Heine V and Samson J H 1980 *J. Phys. F: Met. Phys.* **10** 2609
[43] Heine V and Samson J H 1983 *J. Phys. F: Met. Phys.* **13** 2155
[44] Yang C-H, Koo J, Song C, Koo T Y, Lee K-B and Jeong Y H 2006 *Phys. Rev. B* **73** 224112
[45] Oguchi T, Terakura K and Williams A R 1983 *Phys. Rev. B* **28** 6443
[46] Zaanen J and Sawatzky G A 1987 *Can. J. Phys.* **65** 1262
[47] Solovyev I V and Terakura K 1998 *Phys. Rev. B* **58** 15496
[48] Mazurenko V V, Skornyakov S L, Kozhevnikov A V, Mila F and Anisimov V I 2007 *Phys. Rev. B* **75** 224408
[49] Kugel K I and Khomskii D I 1982 *Sov. Phys.—Usp.* **25** 231
[50] de Brito P E and Shiba H 1998 *Phys. Rev. B* **57** 1539
[51] Solovyev I V 2003 *Phys. Rev. B* **67** 014412
[52] Georges A, Kotliar G, Krauth W and Rozenberg M J 1996 *Rev. Mod. Phys.* **68** 13
[53] Dagotto E 2005 New J. Phys. 7 67
[54] Nagaev E L 1996 Physics—Usp. 39 781
[55] Kodama K, Iikubo S, Shamoto S-I, Belik A A and Takayama-Muromachi E 2007 J. Phys. Soc. Japan 76 124605
[56] Konishi Y, Fang Z, Izumi M, Manako T, Kasai M, Kuwahara H, Kawasaki M, Terakura K and Tokura Y 1999 J. Phys. Soc. Japan 68 3790
[57] Fang Z, Solovyev I V and Terakura K 2000 Phys. Rev. Lett. 84 3169
[58] Ohshima E, Saya Y, Nantoh M and Kawai M 2000 Solid State Commun. 116 73
[59] Uehara M, Mori S, Chen C H and Cheong S-W 1999 Nature 399 560