Interlayer magnetic-frustration–driven quantum spin disorder in the honeycomb compound In$_3$Cu$_2$VO$_9$

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Abstract – In this paper we present the electronic and magnetic properties of the honeycomb compound In$_3$Cu$_2$VO$_9$. We find that the band dispersions display Dirac cone features in the nonmagnetic phase, as observed in graphene. The parent phase is a charge transfer insulator with an energy gap of about 1.5 eV. Singly occupied $d_{3z^2-r^2}$ electrons of copper ions contribute an $S = 1/2$ spin, while vanadium ions show nonmagnetism. The planar nearest-neighbor, next-nearest-neighbor and interplane superexchange couplings of Cu spins are $J_1 \approx 16.2$ meV, $J_2 \approx 0.3$ meV and $J_z \approx 1.2$ meV, suggesting a low-dimensional antiferromagnet rather than a spin liquid. We propose that the magnetic frustration along the $c$-axis leads to a quantum spin disorder in In$_3$Cu$_2$VO$_9$, in accordance with recent experiments.

Introduction. – Atoms in a reduced-dimensional lattice, for example, in a two-dimensional (2D) honeycomb lattice, have low coordinate number and small spin number. Together with magnetic frustration, these electrons may experience strong spin fluctuations and probably form a low-dimensional (low-D) antiferromagnet (AFM), or even exotic spin liquid, or quantum disorder, or a quantum spin liquid, or a quasiquantum spin liquid, or a quantum spin liquid predicted by Meng et al. [1]. Noninteracting or weakly interacting electrons in hexagonal graphene are a typical example of Dirac fermions. It is not very clear how the properties of Dirac fermions evolve with the increase of Coulomb interactions. Therefore, In$_3$Cu$_2$VO$_9$ with hexagonal Cu ions is probably a realistic material to unveil how the electronic correlations affect the Dirac fermions. Moreover, through the magnetic susceptibility and specific-heat measurements, it is hard to distinguish a possible ground state between a low-dimensional AFM and a spin liquid [16]. All of these drive us to explore the electronic properties and magnetism in In$_3$Cu$_2$VO$_9$ by combining the first-principles electronic-structure calculations and analytic methods, for this could provide us with a first insight into this compound.

In this paper, we propose that In$_3$Cu$_2$VO$_9$ is an AFM charge transfer insulator with copper $d_{3z^2-r^2}$ orbitals...
half-filled and contributing $S = 1/2$ spins. Furthermore, we show that the absence of 3D AFM long-range order observed experimentally in In$_3$Cu$_2$VO$_3$ arises from the magnetic frustration of Cu spins along the $c$-axis, leading to a quantum disorder phase.

**Methods and crystal structure.**—We first study the electronic-state properties of the honeycomb compound In$_3$Cu$_2$VO$_3$ by employing the first-principles electronic-structure calculation approach so as to elucidate its ground-state properties. The electronic structure calculations were performed using the self-consistent full-potential linearized augmented plane-wave (FP-LAPW) scheme in the WIEN2k programme package [17]. We use 36 $k$-points in the irreducible part of the first Brillouin zone. The muffin-tin sphere radii are selected to be 2.36, 1.93, and 1.71 a.u. for In, Cu (V), and O in In$_3$Cu$_2$VO$_3$. The plane-wave cutoff parameter $R_{MT}K_{\text{max}}$ was 7.0, and the cutoff energy between the core and valence states was $-7.0$ Ry in all calculations. Exchange and correlation effects were taken into account in the generalized gradient approximation (GGA) by Perdew, Burke, and Ernzerhof (PBE) [18]. In order to explicitly take into account the correlated effect of the 3$d$ electrons of Cu (V) ions, we also performed GGA+$U$ calculations for In$_3$Cu$_2$VO$_3$. The effective Coulomb interaction $U_{\text{eff}} = U_{3d} - J_{3d}$ ($U_{3d}$ and $J_{3d}$ are the on-site Coulomb interaction and Hund’s rule coupling for the transition metal ions, respectively) is used instead of $U$. We take $U_{\text{eff}} = 8.0$ eV for copper and 4.0 eV for vanadium according to similar compounds [19–21].

In order to compare our numerical results with the experimental data, we adopt the experimental structural data of In$_3$Cu$_2$VO$_3$ measured by neutron powder diffraction [14]. This compound has an orthorhombic structure with space group $Cmcm$ and lattice constants $a = 10.0491 \text{ Å}$, $b = 5.8019 \text{ Å}$, and $c = 11.8972 \text{ Å}$, as shown in fig. 1. It is found that In$_3$Cu$_2$VO$_3$ has a honeycomb layered structure with Cu atoms forming a hexagonal net and V atoms in the center of a hexagon. A Cu atom is surrounded by five O atoms in a trigonal bipyramidal environment.

![Fig. 1: (Color online) (a) Unit cell of In$_3$Cu$_2$VO$_3$ ($Cmcm$ space group), and corresponding high-symmetry points in the first Brillouin zone.](image1)

**Results.**—

**Nonmagnetic state.**—We first present the NM electronic structures of In$_3$Cu$_2$VO$_3$ in fig. 2. It shows that the major orbital character of the band structures near $E_F$ is a $3z^2 - r^2$ symmetry of copper 3$d$ orbitals. This Cu 3$d_{3z^2 - r^2}$ orbital in the honeycomb lattice, similar to the $p_z$ orbital of carbon in graphene, contributes an outstanding property of the band structures, i.e., a Dirac cone with the approximately linear spectrum is observed around the $H$-point, as seen in fig. 2. The linear energy spectrum ranges from $-0.2$ to $0.2$ eV. We notice that the original Dirac point around the $K$-point opens a small energy gap, about $0.2$ eV, also as seen in fig. 2, which is attributed to the weak interlayer coupling between Cu/V-O hexagonal planes. Though parts of the empty V 3$d$ orbital are near the top of Cu 3$d_{3z^2 - r^2}$ orbitals, they do not directly hybridize with each other considerably. A part of filled oxygen 2$p$ orbitals close to the bottom of Cu 3$d_{3z^2 - r^2}$ orbitals, and these 2$p$ orbitals also do not considerably mix with 3$d_{3z^2 - r^2}$ orbitals, as can be seen from the partial density of states (PDOS) of In$_3$Cu$_2$VO$_3$ in fig. 3. Thus, the low-energy physics in In$_3$Cu$_2$VO$_3$ could be approximately described by the Cu 3$d_{3z^2 - r^2}$ orbitals across $E_F$.

![Fig. 2: (Color online) Band structures with orbital character of In$_3$Cu$_2$VO$_3$ in the NM situation by the LDA method. We indicate the major orbital component of each band. A fit to the band with Cu 3$d_{3z^2 - r^2}$ orbital character is marked with open circles.](image2)
we further adopt the spin-polarized GGA and correlation-corrected GGA+U schemes to uncover the ground-state properties of strongly correlated In$_3$Cu$_2$VO$_9$. Several kinds of magnetic configurations, ferromagnet (FM), A-type AFM (i.e., interlayer AFM and intralayer FM), G-type (G1- and G2-type) AFM, stripe AFM and zigzag AFM, are considered. Here G1- and G2-type AFM configurations shown in fig. 6 are two different magnetic structures, both of which are derived from a conventional G-type AFM. In comparison with the G1-type AFM structure, the lower Cu/V-O hexagon (or Cu/V-O layer) in the G2-type structure rotates by $\pi/3$ degrees. Thus, the G1-type spin configuration differs from the G2-type one. Our GGA+U numerical results show that the total energy of the NM state is the highest, and those of the G1- and G2-type AFM states are the lowest. Interestingly, we find that the G1- and G2-type AFM states are degenerate. This arises from the interlayer magnetic frustration of Cu spins, as will be discussed in detail later. The total energy difference between the FM and A-type AFM configurations is small, giving a finite $J_c \sim 1.2 \text{meV}$ but non-negligible. The energy difference between the lowest G1(G2)-type AFM and A-type AFM states is about 58.5 meV, suggesting that the AFM magnetic couplings between Cu spins in In$_3$Cu$_2$VO$_9$ are dominant.

To examine the effect of the on-site Coulomb interaction parameter $U$ on the calculation results, we also perform the spin-polarized GGA calculations for the purpose of comparison. The PDOS of In$_3$Cu$_2$VO$_9$ for G1(G2)-type AFM states is shown in fig. 4. It is found that the system is an insulator with an energy gap of 0.4 eV. However, the calculated magnetic moment is only $0.4 \mu_B$, smaller than that observed by the experiment, about $0.5 \mu_B$ [14]. Considering the fact that the LSDA results usually overestimate the magnitude of a magnetic moment, while the experimental results underestimate it
due to the significant disorder and fluctuations in realistic compounds, one can expect that there exists a magnetic moment over $0.5 \mu_B$. Note that since we only considered several types of collinear magnetic configurations with high symmetry in our present work, we cannot exclude the spin canting case. Thus, the reduction of the observed magnetic moment may arise from the canted spins. Further experiments are needed to investigate the possible canted spins in this compound. In a similar system, Cu$_2$V$_2$O$_7$, with $0.73 \mu_B$ for $U_{\text{eff}} = 6.52$ eV [19], the GGA+$U$ calculations are also needed for In$_3$Cu$_2$VO$_9$. We choose the Coulomb parameters lying in a physical parameter range for In$_3$Cu$_2$VO$_9$, i.e., $U_{\text{eff}} = 4.5$–$8$ eV for Cu ions, and $4$ eV for V ions according to the similar compounds, such as Cu$_2$V$_2$O$_7$ [19] and In$_2$VO$_9$ [20], as well as general compounds, such as cuprates and vanadium oxides (V$_2$O$_3$ [21]), etc.

To further uncover the insulating character of In$_3$Cu$_2$VO$_9$, the PDOS for G1(or G2)-type AFM states is plotted within GGA+$U$ as seen in fig. 5. The system is obviously an insulator with an energy gap of $1.5$ eV. We find that oxygen $2p$ orbitals consist of major bands near $E_F$, ranging from $0$ to $-4.0$ eV, while the gravity center of Cu $3d$ orbitals lies far from $E_F$. The center of the spin-up $3d$ orbital lies at about $-5.9$ eV, and that of the spin-down $3d$ orbitals lies at about $-4.8$ eV. This gives rise to the exchange splitting of Cu $3d$ orbitals about $\Delta_{xx} \approx 1.1$ eV, implying that Hund’s rule coupling $J_{3d} = \Delta_{xx}/2S \approx 1.1$ eV.

Note that the charge transfer energy between the O $2p$ orbital and the Cu $3d$ orbital in In$_3$Cu$_2$VO$_9$, $\Delta = \epsilon_{2p} - \epsilon_{3d}$, is smaller than but near the on-site Coulomb interaction $U$ of Cu $3d$ electrons in the physical parameter regime, demonstrating that In$_3$Cu$_2$VO$_9$ is a charge transfer insulator close to the Mott one.

Figure 5 shows that the main DOS of copper lies from $-7$ eV to $-4$ eV, though a tiny portion of $3d$ electrons lies between $-4$ eV and $E_F$ which mainly arises from the hybridization of the Cu $3d$ orbital with the $2p$ orbitals near $E_F$. We find that the orbital ground state is the Cu $3d_{x^2−y^2}$ characteristic, in agreement with the electron spin resonance experiment by Kataev et al. [27]. Moreover, a small but finite DOS distributed from $-6$ eV to $E_F$ is seen in the V $3d$ orbitals, while the DOS of oxygen mainly distributes near $E_F$. Such a strongly correlated character in In$_3$Cu$_2$VO$_9$ is similar to that in the parent phases of high-$T_c$ cuprates. This implies that the doping in O sites can readily affect the transport properties in In$_3$Cu$_2$VO$_9$, and easily drive the system transist to a metallic or a superconducting phase once the hole carriers are doped in oxygen $2p$ bands. Nevertheless, we do not expect that doped In$_3$Cu$_2$VO$_9$ will form the well-known Zhang-Rice singlet in the Cu-O plane of cuprates, since the latter arises from the hybridization between Cu $3d_{x^2−y^2}$ and O $2p$ orbitals, forming delocalized states in the $xy$ plane, while in the former, the $3d_{x^2−y^2}$ orbital mixes with O $2p$ orbital, forming a delocalized state in the $z$-direction. This results in completely different transport properties in doped compounds, as Yan et al. observed in In$_3$Cu$_2$−zCo$_2$VO$_9$ and In$_3$Cu$_2$−zZn$_2$VO$_9$ [16].

Magnetic coupling strengths. The ground-state magnetic properties of In$_3$Cu$_2$VO$_9$ are the central issue of this paper. As described above, our numerical results demonstrate that the stabllest phases are the degenerate G1- and G2-type AFM states. The insulating nature in In$_3$Cu$_2$VO$_9$ suggests that the local spins of cuppers interact through a superexchange couplings mediated via oxygen and vanadium. One expects that the contributions to the NN and NNN Cu-Cu superexchange couplings are ascribed to the direct hopping between $d_{x^2−y^2}$ electrons, the indirect hopping between Cu spins through the $p$-$d$ hybridization of intermediate oxygen anions and through the O-V-O bridge. To quantitatively obtain the superexchange coupling strengths, we utilize the tight-binding parameters obtained in table 1 to estimate the NN and NNN superexchange couplings between Cu spins in the Cu/V-O plane and between the planes, taking the effective Coulomb interaction $U_{3d}$ as $8$ eV. Since In$_3$Cu$_2$VO$_9$ is a charge transfer insulator close to the Mott one, it can be treated properly within the Mott-Hubbard framework in the limit $\Delta \sim U$. A $t/U$ expansion of the Hubbard model, which is justified by the strongly correlated $(t \ll U_{3d})$ regime, is used to obtain an effective $J_1 - J_2 - J_c$ spin $S = 1/2$ model on a honeycomb lattice:

\[
H = J_1 \sum_{\langle i \rangle_{ab}} \vec{S}_i \cdot \vec{S}_j + J_2 \sum_{\langle\langle i \rangle \rangle_{ab}} \vec{S}_i \cdot \vec{S}_j + J_c \sum_{\langle i \rangle_c} \vec{S}_i \cdot \vec{S}_j ,
\]

where $J_1 = 4t_1^2/U - 16t_1^2/U^3$, $J_2 = 4t_2^2/U + 4t_2^2/U^3$ and $J_c = 4t_c^2/U$ are the NN, NNN intralayer and the NN interlayer magnetic couplings, respectively. We find that the intraplane and interplane NN superexchange couplings

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**Fig. 5:** (Color online) PDOS of In$_3$Cu$_2$VO$_9$ for the G1(G2)-type AFM states by the spin-polarized GGA+$U$ method.

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are about $J_1 \approx 16.2\text{ meV}$ and $J_c \approx 1.2\text{ meV}$, respectively; and the intraplane NNN superexchange couplings are about $J_2 \approx 0.3\text{ meV}$.

More long-range magnetic couplings are so small to be negligible. This gives rise to $J_2/J_1 \approx 0.02$, in addition to a rather weak interlayer coupling of $J_c/J_1 \approx 0.07$. In addition, a fit to the specific-heat and magnetic susceptibility data within the Monte Carlo framework suggests that $J_1$ is about 12.1 meV [14,27], which is close to our obtained value of 16.2 meV. Furthermore, the magnetic susceptibility and specific heat of a honeycomb lattice are investigated by the Schwinger boson approach in our recent work [28], which presents a similar behavior observed in $\text{In}_2\text{Cu}_2\text{VO}_9$. For comparison, we also extract the average values of magnetic coupling strengths within the general total energy scheme based on the LDA calculations, and find that the results are consistent with those obtained within the perturbation theory framework in the physical range of the parameter $U_{ad}$. All of these magnetic coupling strengths have been listed in table 1. From the literature available, we find that the magnetic coupling strengths of $\text{In}_2\text{Cu}_2\text{VO}_9$ fall in the parameter range of a 2D Heisenberg AFM [5,29], showing that $\text{In}_2\text{Cu}_2\text{VO}_9$ is an insulator with 2D AFM. As we will illustrate later, such a weak interlayer magnetic coupling and the spin frustration are prevented from the long-range AFM order in $\text{In}_2\text{Cu}_2\text{VO}_9$.

**Remarks and conclusions.** — It is observed experimentally that neither the specific heat nor magnetic susceptibility exhibits an AFM-PM transition [16]: the former is almost $T^2$-dependent, and the latter linearly increases with the increase of temperature. Consequently, one naturally suspects that the ground state of $\text{In}_2\text{Cu}_2\text{VO}_9$ might be a gapless spin liquid phase, a long-time searched exotic quantum phase both theoretically and experimentally, since such a phase in a Kagome lattice also shows similar unusual temperature-dependent behavior in the low-$T$ regime [3,30]. Moreover, a strongly low-D AFM may exhibit similar behaviors [31]. Although both a low-dimensional AFM and a spin liquid have local permanent magnetic moments, and do not display any sign of ordering in specific heat and magnetic susceptibility down to the lowest temperatures despite comparable strong AFM interactions, a low-dimensional AFM could be different from a spin liquid in many aspects. For example, a 2D AFM has a long-range correlation and long-range order at $T = 0\text{ K}$ as well as a short-range one at finite $T$, while a spin liquid only has a short-range correlation, even at $T = 0\text{ K}$; this leads to distinct low-temperature behavior in magnetic susceptibility for a 2D AFM and a spin liquid, etc. Therefore, our theoretical analysis above suggests a 2D AFM ground state rather than a spin liquid, though it is still mysterious why $\text{In}_2\text{Cu}_2\text{VO}_9$ exhibits neither an AFM long-range order in the low-temperature regime nor a Curie-Weiss law in the high-temperature regime [14,16], which is exotic and distinctly different from undoped cuprates.

An earlier experimental study by Möller et al. [14] attributed the absence of a 3D AFM long-range order to the disorder stacking of 2D Cu/V order domains along the $c$-axis. However, from our preceding data and the particular geometry of $\text{In}_2\text{Cu}_2\text{VO}_9$, as an alternative explanation, we propose that it is the strong AFM frustration along the $c$-axis that leads to the absence of the 3D AFM long-range order in $\text{In}_2\text{Cu}_2\text{VO}_9$. As can be seen by the Cu-V geometric configuration among two Cu-V layers in fig. 6, a Cu spin has two NN layers along the $c$-axis, and it has the same distance to other two Cu spins in the upper or lower layer, forming an isosceles triangle which is a notorious spin configuration with magnetic frustration. Our analysis above has shown that both the magnetic couplings of the interlayer and intralayer spins are AFM, indicating the spin fluctuations along the $c$-axis will be very large. Thus, in $\text{In}_2\text{Cu}_2\text{VO}_9$ the intralayer Cu spins are AFM correlated, while the interlayer Cu spins are quantum disordered. Such a frustration scenario could unitedly account for both the presence of a low-D AFM correlation [15] and the absence of a 3D AFM order [14,16,27] in recent experiments.

Furthermore, we apply our frustration scenario to uncover the evolution of the magnetic properties on the Co and Zn dopings in $\text{In}_2\text{Cu}_2\text{VO}_9$, giving a possible explanation of the experimental behavior, as shown in fig. 7. The Zn and Co dopings break the interlayer frustration, while the NM Zn$^{2+}$ ions destroy the intralayer AFM. On the contrary, high-spin-(3/2) Co$^{2+}$ ions enhance it. Thus, the Zn doping induces a weak AFM at low doping, but suppresses the AFM state completely at high doping. In comparison, the Co doping results in a strong AFM with...
large effective magnetic moment. All the results are in accordance with the experimental observations.

In summary, the investigation of the electronic structure and magnetic properties in the quasi-2D honeycomb compound In$_2$Cu$_4$VO$_9$ demonstrates that the undoped phase is a charge transfer insulator with a gap of 1.5 eV. The spin-(1/2) local moment antiferromagnetically interacts and occupies the $3z^2-r^2$ orbital in copper. The tight-binding parameters and estimated magnetic coupling strengths suggest that In$_2$Cu$_4$VO$_9$ is a strongly 2D Néel AFM. We propose that the spin fluctuations arising from the magnetic frustration along the c-axis destroy the 3D AFM long-range order, leading to random stacking of Cu-V layers.

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REFERENCES

[1] Meng Z. Y., Lang T. C., Wessel S., Assaad F. F. and Muramatsu A., Nature, 464 (2010) 847.
[2] Yan S. M., Huse D. A. and White S. W., Science, 332 (2011) 1173.
[3] Saremi S. and Lee P. A., Phys. Rev. B, 75 (2007) 165110.
[4] Vaezi A. and Wen X.-G., arXiv:1010.5744 (2010), arXiv:1101.1662 (2011).
[5] Clark B. K., Abanin D. A. and Sondhi S. L., Phys. Rev. Lett., 107 (2011) 087204.
[6] Wang F., Phys. Rev. B, 82 (2010) 024419.
[7] Liebsch A., Phys. Rev. B, 83 (2011) 055113.
[8] He J., Kou S.-P., Liang Y. and Feng S.-P., Phys. Rev. B, 83 (2011) 205116; He J., Zong Y. H., Kou S.-P., Liang Y. and Feng S.-P., Phys. Rev. B, 84 (2011) 035127.
[9] Lu Y.-M. and Ran Y., Phys. Rev. B, 84 (2011) 024420.
[10] Zhao H. H., Xu C. K., Chen Q. N., Wei Z. C., Qin M. P., Zhang G. M. and Xiang T., Phys. Rev. B, 85 (2012) 134416.
[11] Wang W.-S., Xiang Y.-Y., Wang Q.-H., Fang F. and Lee D.-H., Phys. Rev. B, 85 (2012) 035414.
[12] Wu W., Rachel S., Liu W.-M. and Le Hur K., Phys. Rev. B, 85 (2012) 205102.
[13] Li T., EPL, 97 (2012) 37001.
[14] Möller A., Löw U., Taetz T., Kriener M., Andre G., Damay F., Heyer O., Braden M. and Mydosh J. A., Phys. Rev. B, 76 (2008) 024420.
[15] Yehia M., Vavilova E., Möller A., Taetz T., Löw U., Klingeler R., Kataev V. and Büchner B., Phys. Rev. B, 81 (2010) 060414(R).
[16] Yan Y.-J., Li Z.-Y., Zhang T., Luo X.-G., Ye G.-J., Xiang Z.-J., Cheng P., Zou L.-J. and Chen X. H., Phys. Rev. B, 85 (2012) 085102.
[17] Blaha P., Schwarz K., Madsen G., Kvasnicka D. and Luitz J., Computer Code WIEN2k, an augmented plane wave plus local orbitals program for calculating crystal properties (Karlsruhe Schwarz, Technische Universität Wien, Austria) 2001.
[18] Perdew J. P., Burke K. and Ernzerhof M., Phys. Rev. Lett., 77 (1996) 3865.
[19] Yashima M. and Suzuki R. O., Phys. Rev. B, 79 (2009) 125201.
[20] Wang H. and Schwingenschlögl U., J. Phys.: Condens. Matter, 22 (2010) 416002.
[21] Rodolakis F., Hansmann P., Ruffe J.-P., Toschi A., Haverkort M. W., Sangiovanni G., Tanaka A., Saha-Dasgupta T., Andersen O. K., Held K., Sikora M., Alliot I., Itié J.-P., Baudelet F., Wietek P., Metcalf P. and Marsi M., Phys. Rev. Lett., 104 (2010) 047401.
[22] Andersen O. K., Phys. Rev. B, 12 (1975) 3060.
[23] Andersen O. K. and Saha-Dasgupta T., Phys. Rev. B, 62 (2000) 16219(R).
[24] Mostofi A. A., Yates J. R., Lee Y.-S., Souza I., Vanderbilt D. and Marzari N., Comput. Phys. Commun., 178 (2008) 685.
[25] Kunes J., Arita R., Wissgott P., Toschi A., Ikeda H. and Held K., Comput. Phys. Commun., 181 (2010) 1888.
[26] Andersen O. K., Pawlowska Z. and Jepsen O., Phys. Rev. B, 34 (1986) 5253.
[27] Kataev V., Möller A., Löw U., Jung W., Schittner K., Kriener M. and Freimuth A., J. Magn. & Mater., 290-291 (2005) 310.
[28] Yu Xiang-Long, Liu Da-Yong, Li Peng and Zou Liang-Jian, arXiv:1301.5282 (2013).
[29] Mezzacapo F., Rodolakis F., Hansmann P., Rueff J.-P., Toschi A., Saha-Dasgupta T., Andersen O. K., Held K., Sikora M., Alliot I., Itié J.-P., Baudelet F., Wietek P., Metcalf P. and Marsi M., Phys. Rev. Lett., 104 (2010) 047401.
[30] Andersen O. K., Phys. Rev. B, 12 (1975) 3060.
[31] Andersen O. K. and Saha-Dasgupta T., Phys. Rev. B, 62 (2000) 16219(R).
[32] Mostofi A. A., Yates J. R., Lee Y.-S., Souza I., Vanderbilt D. and Marzari N., Comput. Phys. Commun., 178 (2008) 685.
[33] Kunes J., Arita R., Wissgott P., Toschi A., Ikeda H. and Held K., Comput. Phys. Commun., 181 (2010) 1888.
[34] Andersen O. K., Pawlowska Z. and Jepsen O., Phys. Rev. B, 34 (1986) 5253.
[35] Kataev V., Möller A., Löw U., Jung W., Schittner K., Kriener M. and Freimuth A., J. Magn. & Mater., 290-291 (2005) 310.
[36] Yu Xiang-Long, Liu Da-Yong, Li Peng and Zou Liang-Jian, arXiv:1301.5282 (2013).
[37] Mezzacapo F. and Boninsegni M., Phys. Rev. B, 85 (2012) 060402.
[38] Ran Y., Hermene M., Lee P. A. and Wen X.-G., Phys. Rev. Lett., 98 (2007) 117205.
[39] Oka K., Yamada I., Azuma M., Takeshita S., Sato K. H., Koda A., Kadono R., Takano M. and Shilmakawa Y., Inorg. Chem., 47 (2008) 7355.