Magnetostriction and ferroelectric state in AgCrS$_2$

Sergey V Streltsov$^{1,2}$, Alexander I Poteryaev$^{1,3}$ and Alexey N Rubtsov$^{1,5}$

$^1$ M.N. Miheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, 620137, Ekaterinburg, Russia
$^2$ Ural Federal University, Mira St. 19, 620002 Ekaterinburg, Russia
$^3$ Institute of Quantum Materials Science, Bazhova St. 51, Ekaterinburg 620075, Russia
$^4$ Department of Physics, Moscow State University, Moscow 119991, Russia
$^5$ Russian Quantum Center, Moscow 143025, Russia

E-mail: streltsov@imp.uran.ru

Received 3 December 2014, revised 3 February 2015
Accepted for publication 6 February 2015
Published 30 March 2015

Abstract

The band structure calculations in the GGA+U approximation show the presence of additional lattice distortions in the magnetically ordered phase of AgCrS$_2$. The magnetostriction leads to the formation of long and short Cr–Cr bonds in the case when the respective Cr ions have the same or opposite spin projections. These changes in the Cr lattice are accompanied by distortions of the CrS$_6$ octahedra, which in turn lead to the development of spontaneous electric polarization.

Keywords: delafossites, magnetism, magnetostriction

(Some figures may appear in colour only in the online journal)

1. Introduction

Transition metal oxides and sulfides with a delafossite structure are being actively investigated nowadays due to the diverse physical properties observed in these materials. For example, CuMnO$_2$ has been found to show a quite strong dependence of magnetic properties on doping [1, 2], CuAlO$_2$ is one of the rare $p$-type transparent semiconductors [3, 4] and CuFeO$_2$ has been intensively studied in recent years due to its multiferroicity [5]. Another system with a crystal structure closely related to delafossites, AgCrS$_2$, was recently found to be multiferroic [6]. However, the mechanism of the coupling between the electric and magnetic characteristics in this material is still unknown.

The crystal structure of AgCrS$_2$ is shown in figure 1. Triangular planes of Cr ions are stacked along the $c$ direction. At very high temperatures it is characterized by the space group $R\overline{3}m$, which is centro-symmetric. With a decrease in the temperature to $T_c = 670$ K it transforms into $R\overline{3}m$, which is still of high symmetry but lacking inversion and is thus noncentro-symmetric. However, spontaneous electric polarization is not observed down to Néel temperature, $T_N \approx 41$ K, where a magnetically ordered phase develops [6]. This low temperature phase is characterized by a monoclinic noncentro-symmetric $Cm$ space group and a doubling of unit cell [7]. Nevertheless, the general triangular plane geometry is preserved and can be regarded as distorted high symmetry lattice. The magnetic structure for $T < T_N$ consists of the double ferromagnetic (FM) stripes coupled antiferromagnetically (see figure 4 in [7]). This magnetic order is developed due to the strong antiferromagnetic (AFM) exchange interaction between the third nearest neighbors [8].

The absence of electric polarization in the $R\overline{3}m$ phase is ascribed to the disorder of the Ag$^+$ ions [6], which additionally complicates the analysis of interplay between electric and magnetic characteristics in AgCrS$_2$. Different scenarios were proposed to gain insight into the mechanism of multiferroicity [7, 9], but this riddle is far from being solved.

In the present paper we performed the optimization of the crystal structure obtained previously in the experiments on powder samples of AgCrS$_2$ and found the presence of additional lattice distortions in the magnetically ordered phase. In the direction perpendicular to the magnetic stripe (in the Cr planes) the chromium ions with opposite spins become closer to each other and they are moved apart for the same spin projections. These distortions result in the development of spontaneous electric polarization, which therefore has a magnetostrictive origin.
Crystal structure of AgCrS$_2$. The Cr ions forming triangular planes are shown in blue, while the S and Ag ions are in yellow and gray, respectively. It is important that there are two crystallographically different sulfur ions: Each Ag is connected with one S$_1$, but with three S$_2$, which results in different Cr–S bond lengths.

Figure 1.

2. Calculation details

We used a pseudo-potential Vienna ab initio simulation package (VASP) for the calculation of the electronic and magnetic properties of AgCrS$_2$ [10]. The Perdew–Burke–Ernzerhof [11] version of the exchange-correlation potentials was utilized. The strong Coulomb correlations were taken into account via the GGA+U method [12]. The on-site Coulomb interaction ($U$) and Hund’s rule coupling ($J_{H}$) parameters were taken to be $U = 3.7 \, eV$ and $J_{H} = 0.8 \, eV$ [13, 14]. The integration in the course of the self-consistency was performed over a mesh of 175 k-points in the irreducible part of the Brillouin-zone.

The electric polarization was calculated using the Berry phase formalism [15, 16]. The crystal structures of AgCrS$_2$ were taken from [7]. The results presented in section 3 were obtained for the data corresponding to $T = 10 \, K$ ($Cm$), while in section 4 both $T = 10 \, K$ ($Cm$) and $T = 300 \, K$ ($R3m$) structures were used.

3. Electronic and magnetic properties and lattice distortions

It is interesting to note that oxides based on Cr$^{3+}$ ions are usually Mott insulators [13, 17, 18], where the top of the valence band and the bottom of the conduction band are formed by the Cr 3d states and an increase in the Cr oxidation state of up to 4+ is needed to move them on the verge between the Mott and charge-transfer regimes [14, 19–21]. The density of states calculated within the GGA+U approximation for the experimentally observed magnetic structure are presented in figure 2. An analysis of the GGA+U results shows that Cr 3d$^1$ states are split and the occupied part lies about $-4...-2 \, eV$, while the empty states that form the bottom of the conduction band are at $1.5...2 \, eV$. The minority spin states, Cr 3d$^4$, are totally empty and located at $2...3 \, eV$. The magnetic moment on the Cr ions is $2.9 \, \mu_B$, which is in good accordance with the experimental value of $2.7 \, \mu_B$ [7]. The top of the valence band is formed predominantly by the S 3p states and thus the AgCrS$_2$ is the charge-transfer insulator. This is related to the much larger spatial extension of the S 3p orbitals compared with O 2p. As a result, the charge-transfer energy defined as energy costs for the $d^p \rightarrow d^{p+1}p^5$ transition is drastically decreased in sulfides [22]. The effect of the on-site Coulomb repulsion is also important since it splits partially the occupied Cr 3d states and moves them away from the Fermi level. The band gap in AgCrS$_2$ for values of $U$ used was found to be $\sim 1.2 \, eV$, which is much smaller than in the oxides based on the Cr$^{3+}$ ions (e.g. in Cr pyroxenes the band gap is $\sim 4...5 \, eV$ [23]). This can be again attributed to the decrease in the charge-transfer energy in sulfides.

In the experimental $Cm$ crystal structure each chromium atom has six in-plane nearest neighbors: Two of them lie along the $b$ direction at 3.5 Å distance and four Cr are at 3.48 Å distance [7]. The long bonded along the $b$ direction Cr–Cr ions form a ferromagnetically coupled chain, while these chains are magnetically ordered as $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$ (see figure 4 in [7]). It is important to note that according to the experiment the inter-chain distance remains unaltered regardless of the $\uparrow\downarrow$ or $\uparrow\downarrow$ magnetic ordering of different chains. Naively thinking one may expect that magnetostriiction differentiates the distances between the FM ($\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$) and AFM ($\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$) coupled chains and therefore the crystal structure could be somewhat different from the one reported previously.

In order to clarify the discrepancy between the experiment and theoretical considerations we carried out the structural optimization of the low temperature phase using the GGA+U method. The total energy calculations for the experimental
distortions in the two neighboring CrS₆ octahedra are different, the corresponding electric polarization. Note that since the \( d_{S} \) and \( d_{S}^{\perp} \) the double stipes (\( \uparrow\uparrow \downarrow \downarrow \)) is shown. The black arrows show the spin order \( d_{S1} \neq d_{S2} \neq d_{S2} \neq d_{S2} \). (b) The distorted structure and the corresponding electric polarization. Note that since the distortions in the two neighboring CrS₆ octahedra are different, \( P \) and \( P' \) do not compensate each other.

Figure 3. (a) Distortions \( d_{S1}, d_{S2}, d_{S2}, d_{S2} \) (gray dashed arrows) which appear in the experimentally observed double stripe AFM order due to magnetostriction. The direction perpendicular to the double stipes (\( \uparrow\uparrow \downarrow \downarrow \)) is shown. The black arrows show the spin order \( d_{S1} \neq d_{S2} \neq d_{S2} \neq d_{S2} \). (b) The distorted structure and the corresponding electric polarization. Note that since the distortions in the two neighboring CrS₆ octahedra are different, \( P \) and \( P' \) do not compensate each other.

parameters show that the double stripe AFM order does not correspond to the ground state, being 1.7 meV/\( \text{f.u.} \) higher than the FM state. The relaxation of the atomic positions and the lattice parameters dramatically changes this situation, stabilizing the double stripe magnetic structure and making this magnetic order the lowest in total energy.

An analysis of the relaxed atomic positions for the double stripe AFM structure shows that the Cr–Cr distance along the stripe stays the same, \( d_{\parallel} = 3.5 \AA \), while in the perpendicular directions they change substantially: Cr–Cr bonds with the same spin projection are stretched, \( d_{\parallel}^{\uparrow\uparrow} = d_{\parallel}^{\downarrow\downarrow} = 3.52 \AA \) and with opposite spins they are shrunk, \( d_{\parallel}^{\uparrow\downarrow} = 3.44 \AA \) (see figure 3). However, the relaxation does not lead to the corrugation of the Cr planes, leaving the average Cr–Cr distance the same (3.48 Å) in the directions perpendicular to the stripe. Thus, the effect of the magnetostriction for the Cr–Cr bond lengths exceeds \( d_{\parallel} = d_{\parallel}^{\uparrow\uparrow} - d_{\parallel}^{\downarrow\downarrow} \sim 0.04 \AA \) for the given \( U \). For the FM order the relaxation leads to minor changes in the crystal structure.

It has to be noted that the effect of magnetostriction depends strongly on the value of the on-site Coulomb repulsion parameter \( U \). For example, the decrease in \( U \) on 1 eV results in an increase in \( d_{\parallel} \) (up to 0.05 Å). One possible explanation could be that we gain magnetic energy, moving some of the Cr nearest neighbors closer together. For short Cr–Cr pairs the corresponding exchange interaction has to be AFM, since the direct exchange should dominate over other contributions in the edge sharing geometry [8]. This is exactly observed in the present calculations: Cr ions having opposite spin projections become closer. Moreover, a decrease in the Coulomb interaction parameter increases this effect since a direct exchange is inversely proportional to it, \( \sim 1/U \). The gain in magnetic energy due to the direct exchange in \( \uparrow \downarrow \) pairs is compensated by the growth of the elastic energy and the decrease in the magnetic energy gain in \( \uparrow \uparrow \downarrow \downarrow \) Cr pairs, so that an exact value of \( \delta d_{\parallel} \) depends on the details of the different internal parameters of the system.

It was found in [8] that in the LSDA (local spin density approximation) the double stripe AFM structure in AgCrS₂ is stabilized due to the strong AFM exchange coupling between the third nearest neighbours. While the magnetostriction, as explained previously, will certainly modify the nearest neighbour interaction, the exchange to the third nearest neighbours will not be changed drastically because of the unaltered average distances in the chromium plane.

4. Electric polarization

For the calculation of the electric polarization (\( P \)) one needs to choose a reference structure and find the difference (\( \delta P \)) in polarizations for the given and reference structures [24]. One usually takes the high temperature centro-symmetric lattice as the reference. However, as explained previously, in AgCrS₂ the polarization appears at the transition between two noncentro-symmetric structures, \( R3m \) and \( Cm \). Therefore, in spite of the fact that the real reason for the absence of electric polarization in the intermediate temperature \( R3m \) structure is unknown [6], we are forced to consider this structure as the reference.

The transition from the paraelectric to ferroelectric state is accompanied by the transition from paramagnet to AFM with the formation of the long-range magnetic order. The paramagnetic state having local spins and short-range magnetic correlations cannot easily be simulated in the GGA or GGA+U calculations (only using such sophisticated techniques as averaging over different spin configurations [25]). Neither could the nonmagnetic state be used, since the electronic configuration of each Cr⁵⁺ ion would not be (\( d_{\uparrow} \uparrow \uparrow \) ), but (\( d_{\uparrow} \uparrow \downarrow d_{\downarrow} \downarrow \downarrow \) ) (\( d_{\uparrow} \downarrow \downarrow d_{\downarrow} \uparrow \uparrow \) ), which is quite unnatural because of the absence of the local spin. The isotropic AFM state (all Cr neighbors are antiferromagnetically coupled), which would be the best to simulate a paramagnet, is also impossible due to the frustrated triangular lattice. Therefore, we simulate the reference paraelectric state by using the \( R3m \) crystal structure with the FM order.

At the first stage we calculate \( \delta P \) due to the appearance of the double stripe AFM order in the \( R3m \) structure, relaxing the atomic positions for both the double stripe (2S) AFM and FM orders. This results in \( |\delta P_{2S, FM}| \sim 2600 \mu \text{C/m}^2 \) and the polarization was found to be directed perpendicular to the Cr triangular planes (i.e. along the rhombohedral c axis). We also checked that the use of the antiferromagnetically coupled AFM (\( \uparrow \downarrow \uparrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downar
in the temperature structure and found that $|\delta P_{2S\rightarrow FM}| \sim 2800 \mu C m^{-2}$, i.e. practically does not change. Moreover, an additional calculation for the $R3m$ structure, but with fixed ionic positions (i.e. there is only an electronic contribution to the polarization) gives $|\delta P_{2S\rightarrow FM}^{elec}| \sim 1900 \mu C m^{-2}$. That is, it is a redistribution of the electronic charge density due to the double stripe AFM structure that mainly leads to the development of the spontaneous electric polarization in the low temperature phase of AgCrS$_2$. The lattice follows this tendency and changes the absolute value of the polarization.

The double stripe magnetic structure was shown to induce the ferroelectric state due to the specific lattice distortions in CdV$_2$O$_4$ [26], which seems to be related with the orbital-selective behavior [27, 28]. While the crystal structure is quite different in the case of AgCrS$_2$ (defaolfusite-like instead of spinel), the microscopic mechanism beyond the ferroelectric state is similar.

In the $R3m$ crystal structure there are two inequivalent sulfur-sulfur bond lengths [7]. In effect, already in the experimental $R3m$ structure the Cr-S$_1$-Cr and Cr-S$_2$-Cr triangles (formed by two neighboring Cr and one of the common S) are also different in terms of angles and bond lengths Cr-S, as shown in figure 3. The magnetostriction results in the formation of short ($d_{11}^1$) and long ($d_{11}^1$) metal–metal bonds (see figure 3). As a result, the two neighboring Cr↑-S$_1$-Cr↑ and Cr↑-S$_1$-Cr↓ triangles turn out to be differently distorted (the same is valid for the two adjacent triangles with S$_2$ ions). These $d_S$11, $d_S$12, $d_S$21, $d_S$22 distortions do not compensate each other, which leads to non-zero electric polarization. It has to be noted that while this mechanism is based on specific atomic displacements, the distortions by themselves are triggered by different charge-density distributions for the ↑↑ (↓↓) and ↑↓ bonds.

Albeit the magnetostriction strongly modifies all bond lengths, both Cr-S$_1$-Cr and Cr-S$_2$-Cr triangles remain isosceles, as shown in figure 3(b). Therefore, there is no component of the electric polarization along the Cr–Cr bonds. In contrast, since all the displacements $d_{Sij}$ are different in the two neighboring plaquettes (Cr↑-S$_1$-Cr↑ and Cr↑-S$_1$-Cr↓), there are two resulting polarizations $\vec{P}$ and $\vec{P'}$, which lie along the planes of plaquettes, perpendicular to the Cr–Cr bonds. Each CrS$_6$ octahedron from the double chain (AFM double chain) shares its edges with two neighboring octahedra and the net polarization is directed nearly perpendicular to the CrS$_2$ plane, as shown in figure 4.

5. Conclusions

The total energy calculations in the GGA+U approximation for the low temperature $Cm$ crystal structure of the AgCrS$_2$ compound show an importance of the atomic relaxation in setting the experimentally observed magnetic order as a ground state. The relaxed atomic positions for the Cr ions display the changes in distances between the FM chains that coupled ferro- and antiferromagnetically. Therefore, on the basis of the first principles calculations, we predict the existence of a magnetostriction effect in this material which was not observed in experiment [7]. The evaluated electric polarization is mostly due to an electronic rather than structural origin and it is much larger than $20 \mu C m^{-2}$ measured experimentally [6]. This discrepancy can be partially explained by the improper ferromagnetic (not paramagnetic) reference point (which we are forced to use) to calculate the initial polarization. The calculations that treat properly the insulating nature of material at all temperatures and paramagnetism with local moments at high temperatures and long-range magnetic order at low temperatures can be done within the DFT+DMFT method. In this case one would expect that the calculated value of the electric polarization will be reduced. At the same time, the experimental estimation of the electric polarization was obtained on the polycrystalline samples [6], which are known to provide substantially smaller values than in single crystals, due to the features of the pyroelectric measurements, see e.g. [29–32]. The use of polycrystalline samples could also explain the absence of the magnetostriction effect in experiment. Therefore, the DFT+DMFT calculations as well as the refined measurements on single crystal samples are required for further investigation of the electronic and magnetic properties of AgCrS$_2$.

Acknowledgments

We are grateful to A Ushakov and especially to G Giovannetti for their various discussions on the physical properties of AgCrS$_2$ and the calculation of the electric polarization in this material. AIP thanks the Russian Quantum Center for their hospitality. This work is supported by the Russian Foundation for Basic Research project 13-02-00374-a, 13-02-00050-a and 14-02-01219-a, by the Ministry of Education and Science of Russia (grant MK 3443.2013.2), by the Ural Branch of Russian Academy of Science (project 15-8-2-4) and the Samsung corporation via the GRO program.

References

[1] Poienar M et al 2011 Chem. Mater. 23 85–94
[2] Ushakov A V, Streltsov S V and Khomskii D I 2014 Phys. Rev. B 89 024406
[3] Benko F and Koffyberg F 1984 J. Phys. Chem. Solids 45 57–9

Figure 4. Two net electric dipole moments (shown in blue) in the two Cr$_2$S$_3$ plaquettes form a net polarization (shown in red), which is directed nearly perpendicular to the CrS$_2$ plane. The plaquettes do not lie along the same plane (in contrast to figure 3). The blue and green balls correspond to the Cr ions with different spin projections.
[4] Laskowski R, Christensen N, Blaha P and Palanivel B 2009 Phys. Rev. B 79 165209
[5] Ye F, Ren Y, Huang Q, Fernandez-Baca J, Dai P, Lynn J and Kimura T 2006 Phys. Rev. B 73 220404
[6] Singh K, Maignan A, Martin C and Simon C 2009 Chem. Mater. 21 5007–9
[7] Damay F, Martin C, Hardy V, André G, Petit S and Maignan A 2011 Phys. Rev. B 83 184413
[8] Ushakov A, Kukusta D, Yaresko A and Khomskii D 2013 Phys. Rev. B 87 014418
[9] Damay F, Petit S, Braendlein M, Rols S, Ollivier J, Martin C and Maignan A 2013 Phys. Rev. B 87 134413
[10] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[11] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[12] Anisimov V I, Aryasetiawan F and Lichtenstein A I 1997 J. Phys.: Condens. Matter 9 767
[13] Streltsov S V and Khomskii D I 2008 Phys. Rev. B 77 064405
[14] Streltsov S V, Korotin M A, Anisimov V I and Khomskii D I 2008 Phys. Rev. B 78 054425
[15] King-Smith R D and Vanderbilt D 1993 Phys. Rev. B 47 1651
[16] Resta R 1994 Rev. Mod. Phys. 66 889
[17] Matsuno J, Okimoto Y, Kawasaki M and Tokura Y 2005 Phys. Rev. Lett. 95 176404
[18] Sarma D, Maiti K, Vescovo E, Carbone C, Eberhardt W, Rader O and Gudat W 1996 Phys. Rev. B 53 13369–73
[19] Korotin M, Anisimov V, Khomskii D and Sawatzky G 1998 Phys. Rev. Lett. 80 4305
[20] Tsirlin A A, Rabie M G, Efimenko A, Hu Z, Saez-Puche R and Tjeng L H 2014 Phys. Rev. B 90 085106
[21] Komarek A C et al 2008 Phys. Rev. Lett. 101 167204
[22] Bocquet A E, Mizokawa T, Saitoh T, Namatame H and Fujiomi A 1992 Phys. Rev. B 46 3771
[23] Streltsov S V, McLeod J, Moewes A, Redhammer G J and Kurmaev E Z 2010 Phys. Rev. B 81 045118
[24] Spaldin N 2012 J. Solid State Chem. 195 2
[25] Medvedeva J E, Korotin M A, Anisimov V I and Freeman A 2002 Phys. Rev. B 65 172413
[26] Giovannetti G et al 2011 Phys. Rev. B 83 060402
[27] Streltsov S V 2015 J. Magn. Magn. Mater. in press doi:10.1016/j.jmmm.2014.10.150
[28] Streltsov S V and Khomskii D I 2014 Phys. Rev. B 89 161112
[29] Seki S, Onose Y and Tokura Y 2008 Phys. Rev. Lett. 101 067204
[30] Kimura K, Nakamura H, Kimura S, Hagiwara M and Kimura T 2009 Phys. Rev. Lett. 103 107201
[31] Singh K, Caignaert V, Chapon L C, Pralong V, Raveau B and Maignan A 2012 Phys. Rev. B 86 024410
[32] Caignaert V, Maignan A, Singh K, Simon C, Pralong V, Raveau B, Mitchell J F, Zheng H, Huq A and Chapon L C 2013 Phys. Rev. B 88 174403