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Thermodynamic properties and neutron diffraction studies of silver ferrite $AgFeO_2$

A Vasiliev[1], O Volkova[1], I Presniakov[1], A Baranov[1,2], G Demazeau[2], J-M Broto[3], M Millot[3], N Leps[4], R Klingeler[4], B Büchner[4], M B Stone[5] and A Zheludev[6]

[1] Moscow State University, 119991 Moscow, Russia
[2] Institut de Chimie de la Matière Condensée de Bordeaux, CNRS, Universite de Bordeaux, 86 Avenue Dr Schweitzer, 33608 Pessac, France
[3] Laboratoire National des Champs Magnetiques Intenses (LNCMI)—CNRS UPR 3228, Universite de Toulouse, 143 Avenue de Rangueil, 31400 Toulouse, France
[4] Leibniz Institute for Solid State and Materials Research, IFW Dresden, 01171 Dresden, Germany
[5] Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831, USA
[6] Laboratory for Neutron Scattering, Swiss Federal Institute of Technology Zurich and Paul Scherrer Institute, 5232 Villigen, Switzerland

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Abstract

We present thermodynamic and neutron scattering data on silver ferrite $AgFeO_2$. The data imply that strong magnetic frustration $\Theta/T_N \sim 10$ and magnetic ordering arise via two successive phase transitions at $T_2 = 7$ K and $T_1 = 16$ K. At $T < T_2$, two metamagnetic phase transitions at $B_1 \sim 14$ T and $B_2 \sim 30$ T can be identified through the change of slope in the magnetization curve measured up to 53 T. These transitions roughly correspond to an eighth and a quarter of the saturation magnetizations. Unlike for the 'classical' delafossite $CuFeO_2$, the wavevector of the magnetic structure is independent of temperature both at $T < T_2$ and at $T_2 < T < T_1$.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Owing to their numerous applications as catalysts and batteries, luminescent materials and transparent conductors the delafossite-type oxides ABO_2 have been studied very intensely. The specific fields of use for these compounds are determined by their chemical composition. The A-site cations with completely filled d orbitals, $Cu^+(3d^{10})$ and $Ag^+(4d^{10})$, are most appropriate for applications in optics, while the B-site cations with partially filled d orbitals are important elements for the development of batteries and catalysts (see, e.g., the review [1] and references therein). Since either one or two cationic positions in the delafossites could be occupied by the transition metal ions, the issue of magnetism in these quasi-two-dimensional compounds is also important, so that another powerful impetus to their study is the physics of strongly frustrated magnetic systems [2].

The most studied member in the ABO_2 family is the 'delafossite' itself, i.e. $CuFeO_2$ (see recent papers [3–5] and references therein). In this compound, the Cu^{1+} ions do not exhibit a magnetic moment, while the Fe^{3+} ($3d^5$) ions with half-filled 3d orbitals possess a spin moment $S = 5/2$ and no orbital moment. This fact suggests their Heisenberg-type character. The structure and the orbital configuration imply magnetic interactions of antiferromagnetic nature which frustration is expected to be removed by the formation of a non-collinear 120° magnetic structures within the triangular FeO_6 layers. These structures were found indeed in chromium-based delafossites $LiCrO_2$ [6] and $CuCrO_2$ [7].

It turned out, however, that the 'classical' delafossite $CuFeO_2$ exhibits an Ising-type character which is quite unexpected for the Fe^{3+} ions [8, 9]. The neutron scattering studies present evidence that its ground state is a collinear commensurate 4-sublattice ($\uparrow\uparrow\downarrow\downarrow$) structure with wavevector (1/4, 1/4, 3/2). Upon heating, the system transforms into a sinusoidal amplitude modulated phase at $T_2 = 11$ K. In this phase, the four sublattice magnetic structure is replaced by an incommensurate phase, in which the magnetic Bragg reflections occur at positions $(q, q, (6m+3)/2)$, where m is an integer and the value of q is temperature dependent and ranges

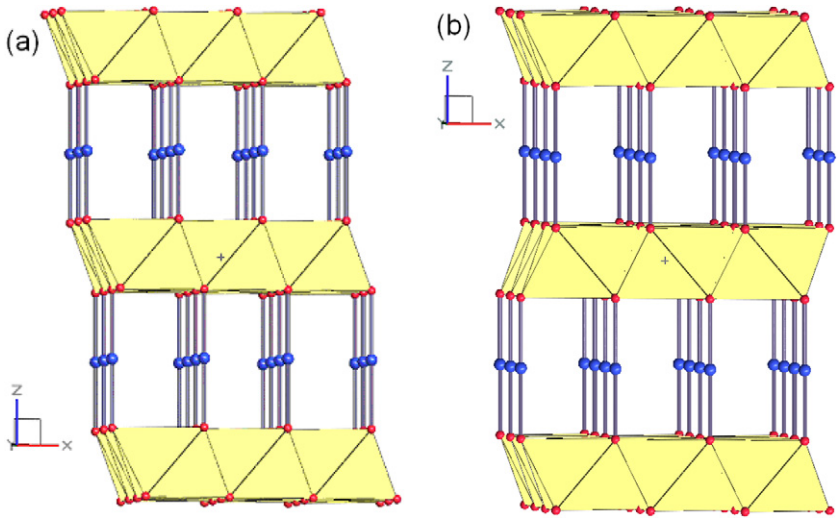

Figure 1. The polyhedral representation of the crystal structures of 3R (a) and 2H (b) polytypes of $AgFeO_2$. Yellow octahedra are oxygen (red (smaller) spheres) coordinated Fe sites. Blue (larger) spheres are Ag sites.

Table 1. Crystal lattice parameters of $AgFeO_2$ and $CuFeO_2$.

Compound	Crystal group	a (Å)	c (Å)	Reference
$AgFeO_2$-2H	$P6_3/mmc$	3.0390	12.395	[19]
$AgFeO_2$-3R	$R\bar{3}m$	3.0391	18.590	[18]
$CuFeO_2$	$R\bar{3}m$	3.0351	17.166	[20]

from 0.19 to 0.225. This collinear incommensurate phase transforms into a paramagnetic phase at $T_1 = 14$ K [10, 11]. The magnetic structure of $CuFeO_2$ is quite sensitive to external magnetic fields. A succession of metamagnetic phase transitions has been observed in a field-oriented powder. Monte Carlo simulations suggest that the successive critical magnetic fields correspond to transitions between various stable magnetic configurations [12]. The importance of magnetoelastic coupling in $CuFeO_2$ was revealed recently in synchrotron x-ray diffraction [13–15] and ultrasonic velocity measurements under external magnetic field [16, 17].

In the vast family of delafossites ABO_2, one of the least studied members is the silver ferrite $AgFeO_2$. To our knowledge, the available information on its properties is limited to the structural data on the two polytypes, i.e. rhombohedral 3R (space group $R\bar{3}m$) [18] and hexagonal 2H (space group $P6_3/mmc$) [19], crystal structures. The silver ferrite consists of alternate A layers of two-dimensional close-packed silver $Ag^+(4d^{10})$ ions in the dumbbell O–Ag^+–O coordination and B layers of slightly distorted edge-sharing ($Fe^{3+}O_6$) octahedra. The 3R and 2H polytypes differ by the stacking variants, as shown in figure 1. The crystal structure parameters of the 3R and 2H polytypes of $AgFeO_2$ [18, 19] along with those of $CuFeO_2$ [20] are given in table 1. Having the same closed shell electronic configuration of the A layer as $CuFeO_2$, the silver ferrite is a semiconductor, which was proven experimentally [20], but electronic band structure calculations are still debated [21–23].

Despite the fact that silver ferrite $AgFeO_2$ belongs to the already known and well studied delafossites the investigation of every new member in this family may shed new light on the basic properties of these heavily frustrated magnets. The goal of our study was to provide characterization of the local structure and the magnetic behavior of the $AgFeO_2$ ferrite through neutron diffraction techniques and measurements of its thermodynamic properties in the range 1.8–300 K and magnetic fields up to 53 T.

2. Experimental details

Since the binary oxide of silver Ag_2O decomposes at about 300 °C, a single step solid-state synthesis of $AgFeO_2$ in open air is impossible. This difficulty can be overcome using a low temperature or closed reaction system. In the present study, a mixture of Ag_2O and Fe_2O_3 in equal ratio was placed into a Pt container and fired in an oxygen atmosphere at 700 °C for 24 h at 0.15 MPa in a high pressure chamber.

The powder x-ray diffraction pattern of $AgFeO_2$, collected with Cu Kα radiation, is shown in figure 2. It indicates that the sample consists primarily of the 3R polytype, with a small amount of admixed 2H polytype. The x-ray pattern obtained is very similar to that of $AgFeO_2$ prepared by means of hydrothermal synthesis [1]. The magnetic susceptibility χ was measured at $B = 0.1$ T by means of a Quantum Design MPMS SQUID magnetometer. The measurements of magnetization M up to 53 T were performed in pulsed magnetic field. The specific heat C was studied in a Quantum Design PPMS in magnetic field up to 9 T.

The neutron diffraction measurements were performed using the HB1A fixed incident energy (14.62 meV, $\lambda = 2.3567$ Å) triple axis spectrometer located at Oak Ridge National Laboratory's High Flux Isotope Reactor. The sample consisted of approximately 0.8 g of $AgFeO_2$ powder loaded into an aluminum can with helium exchange gas. Measurements in the range 1.8–30 K were made with scanning wavevector transfer, Q, in 2-axis mode of the instrument with the analyzer turned orthogonal to the scattered beam.

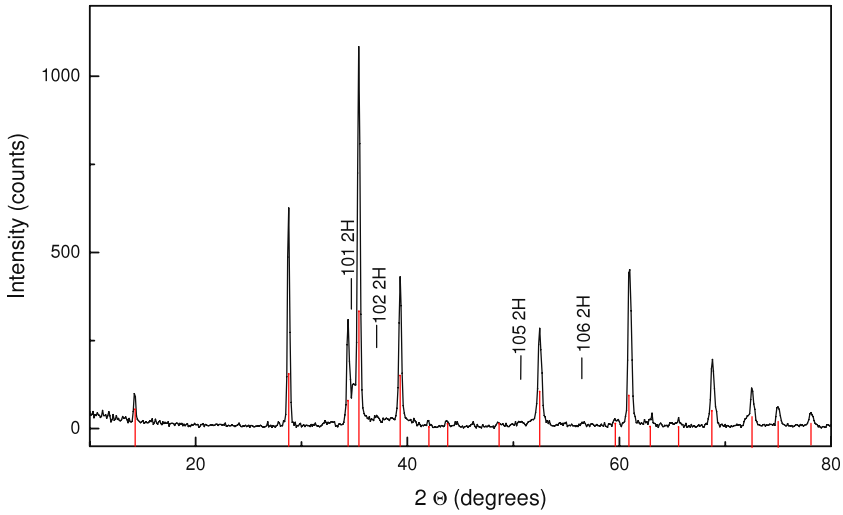

Figure 2. X–ray diffraction pattern of the $AgFeO_2$ powder sample consisting primarily of the 3R polytype, with a small amount of admixed 2H polytype. Red vertical lines correspond to indexed peaks of the 3R polytype based upon the structure described in [18]. Black vertical markers and text correspond to peak positions and indices of the 2H polytype based upon the structure described in [19].

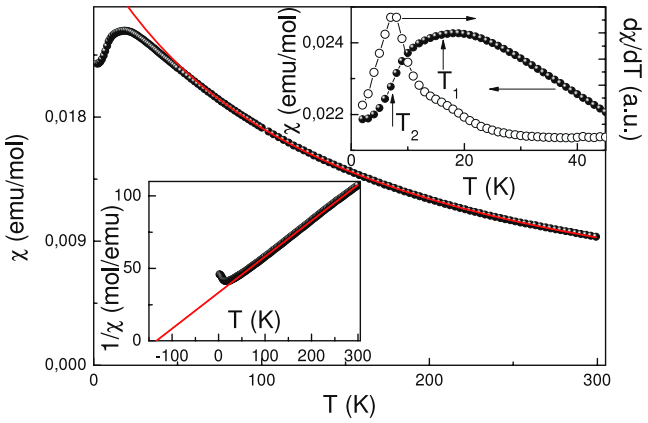

Figure 3. Temperature dependent magnetic susceptibility of $AgFeO_2$. Measurements were made in an applied field of $B = 0.1$ T. The lower inset represents an inverse magnetic susceptibility, while the upper inset enlarges the low temperature region. The solid lines in the main panel and in the lower inset are the Curie–Weiss law. The positions of arrows in the upper inset correspond to anomalies in the specific heat of $AgFeO_2$ at $T_2 = 7$ K and $T_1 = 16$ K.

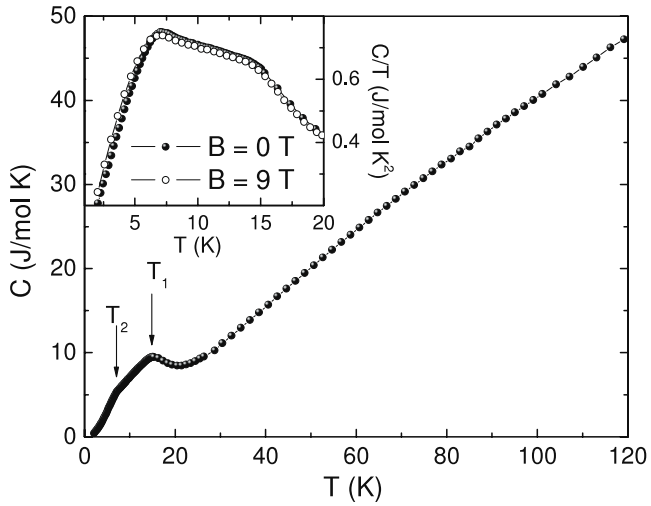

Figure 4. The temperature dependence of the specific heat of $AgFeO_2$. The inset represents an enlarged low temperature region plotting C/T with curves taken at 0 and 9 T magnetic fields. The arrows indicate the successive magnetic phase transitions at $T_2 = 7$ K and $T_1 = 16$ K.

3. Results

The temperature dependence of the magnetic susceptibility $\chi(T)$ of $AgFeO_2$ is shown in figure 3. As follows from the lower inset to figure 3, in a wide temperature range, 70 K $< T <$ 300 K, it obeys the Curie–Weiss law with a negative Weiss temperature $\Theta = -140$ K and an effective magnetic moment $\mu_{\text{eff}} = 5.77\ \mu_B$. This value is slightly lower than the value expected for Fe^{3+} ions with spin-only moments $S = 5/2$, $\mu_{\text{eff}} = 5.92\ \mu_B$. At low temperatures, the magnetic susceptibility drops for about 10% revealing an irregular behavior in the range 2–20 K, as shown in the upper inset to figure 3.

In principle, one might speculate that the broad maximum in $\chi(T)$ dependence is a manifestation of reduced dimensionality and correlation effects in magnetically frustrated layers of FeO_6 octahedra. The specific heat C data, shown in figure 4, indicate, however, that there are clear specific heat anomalies associated with phase transitions at $T_2 = 7$ K and $T_1 = 16$ K. This behavior is highlighted by the C/T data in the inset of figure 4, which also shows that an external magnetic field of 9 T has only a negligible effect on the entropy changes.

At $T < T_2$, the results of pulsed magnetic field measurements, shown in figure 5, indicate two metamagnetic transitions at $B_1 \sim 14$ T and $B_2 \sim 30$ T roughly corresponding to 1/8 and 1/4 of saturation magnetization. The anomalies in the magnetization curve are associated with a small hysteresis when measuring as a function of increasing and decreasing

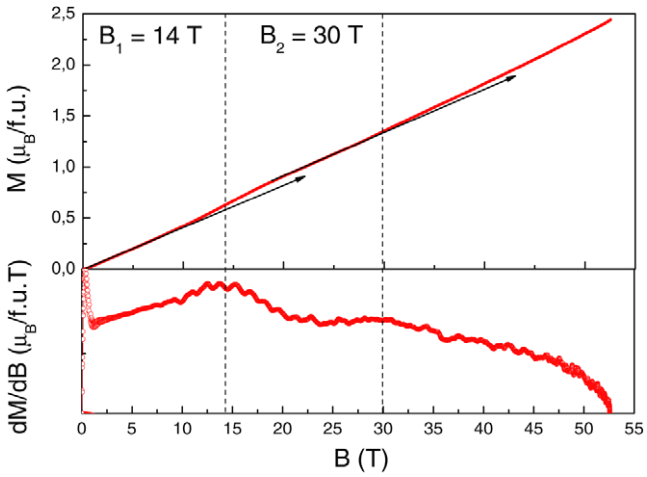

Figure 5. The magnetization of $AgFeO_2$ measured in pulsed magnetic field at 2 K. Black arrows are guides for an eye. The values of critical magnetic field B_1 and B_2 were obtained from the broad maxima in the derivative dM/dB for increasing magnetic fields.

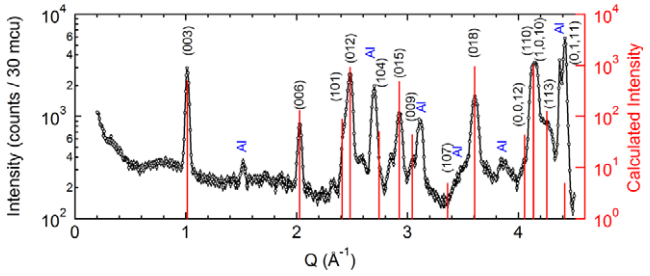

Figure 6. Scattering intensity versus Q for the $T = 30$ K measurement of $AgFeO_2$. Data points are plotted as lines between open circles to illustrate measured points density. Error bars are shown and are typically smaller than the symbol size. Right axis is the calculated scattering intensity (logarithmic scale and arbitrary units) based upon the lattice parameters given in [18]. There are several very weak peaks which are indexed based upon them being due to the aluminum sample holder (Al) or cryostat. Count rates are in units of mcu (monitor count units) where the beam monitor was placed in the incident beam and 1 mcu $\sim$ 1 s.

magnetic field. This feature hence implies a first order nature of these metamagnetic phase transitions associated evidently with transformations in the magnetic subsystem of $AgFeO_2$. Experimentally, the derivative of the magnetic flux by the induced voltage in compensated pick-up coils was measured, as shown in the lower panel of figure 5. From this signal up to 53 T and the measurements of the reference signal without sample within the pick-up coils, the magnetization curve $M(B)$ was integrated.

The neutron diffraction spectra of $AgFeO_2$ were measured in the range 1.8–30 K, the results of measurement at 30 K are shown in figure 6. The nuclear diffraction peaks are consistent with those calculated based upon the hexagonal lattice constants of [18] with space group $R\bar{3}m$. Figure 7 shows the temperature dependence of scattering intensity versus Q characterizing diffraction measurements of $AgFeO_2$ for a series of temperatures focusing on smaller wavevectors. Additional diffraction peaks at small wavevectors appear as the temperature is reduced. This is consistent with these reflections being magnetic in origin. Additional diffraction peaks are measured in the vicinity of 0.75–1 $Å^{-1}$ and in the vicinity of 1.75 $Å^{-1}$. There appears to be two magnetic transitions: one at about $T_2 = 7$ K and another at about $T_1 = 16$ K. We do not observe any significant shift in the position of these peaks as a function of temperature.

We have calculated the wavevectors of potential magnetic Bragg peaks for hexagonal symmetry of the undistorted $R\bar{3}m$ space group for $h = \frac{m}{\delta}$, $k = \frac{n}{\delta}$, and $l = \frac{p}{\varepsilon}$, where m, n, and p are integers and combinations of δ and ε being 2, 3 or 4. The lowest wavevector magnetic peak at $Q = 0.812(6)$ $Å^{-1}$ for $T < T_2$ indexes well to (1/3 0 1/2) or an equivalent hexagonal wavevector ($Q = 0.814$ $Å^{-1}$). The next clear magnetic wavevector at $Q = 0.953(2)$ $Å^{-1}$ for $T_2 < T < T_1$ indexes well to (2/3 0 2) or an equivalent hexagonal wavevector ($Q = 1.729$ $Å^{-1}$). Unfortunately, the small quantity of powder sample and the likelihood of many overlapping peaks makes it difficult to index the magnetic peaks at larger wavevectors with certainty. We do not find an analogous peak at the (1/4 1/4 3/2) wavevector as is observed in the $CuFeO_2$ delafossite. Based upon the indexed peaks at small wavevectors, it is likely that the ordered magnetic structures are 120° spirals with different basis vectors in the two portions of the magnetic phase diagram. Upon lowering temperature, the additional peaks associated with the formation of long-range magnetic order appear at T_1 and are seen down to T_2. At T_2 these peaks disappear, but new ones appear at different wavevectors. In a narrow range around T_2 the peaks corresponding to two different magnetic phases coexist.

4. Discussion

In general, the behavior of silver ferrite resembles strongly that of 'classical' delafossite $CuFeO_2$. Similar to the latter compound, the $AgFeO_2$ exhibits two phase transitions at low temperatures, corresponding to the formation of different magnetic structures below T_1 and in the range $T_2 < T < T_1$. Unlike the situation in $CuFeO_2$ the wavevector of the magnetic structure in the range $T_2 < T < T_1$ appears to be temperature independent. The specific heat data show that a moderate magnetic field has no significant effect on the entropy changes. It seems that the exchange interaction parameters in $AgFeO_2$ exceed the corresponding values in $CuFeO_2$. The Weiss temperature $\Theta \sim -140$ K in the former compound is to be compared with the Weiss temperature $\Theta \sim -70$ K in the latter compound [9]. The silver ferrite appears to be more frustrated since the ratio of Weiss temperature Θ and magnetic ordering temperature T_2 in $AgFeO_2$ is about 10, while it is about 5 in $CuFeO_2$. This change in the energy scale is reflected in a higher value of the first metamagnetic transition field in silver ferrite, i.e. $B_1 = 14$ T, as compared with that in copper ferrite which amounts to 8 T [12].

To explain the apparent Ising-like character of the Fe^{3+} ions and the formation of the collinear magnetic structures in $CuFeO_2$ at low temperatures the presence of defect ions

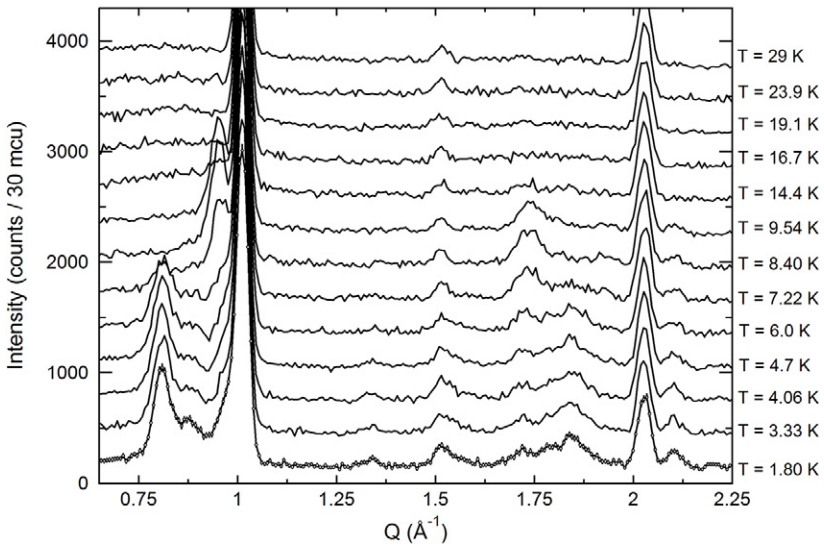

Figure 7. Scattering intensity versus Q for $AgFeO_2$ measured at different temperatures. Data are plotted over a narrow range of wavevector transfer to illustrate regions of magnetic scattering intensity. Data have been offset by multiplies of 300 counts along the vertical axis for presentation. Individual point symbols with error bars are shown for the $T = 1.8$ K data.

Fe^{2+} and Cu^{2+} created by oxygen deficiency and oxygen excess, respectively, was postulated. The electron structure analysis [24] suggests that these defect ions generate uniaxial magnetic moments along the c-axis and hence induce the surrounding Fe^{3+} ions to orient their moments along the c-axis.

The applicability of the Ising model to the description of the triangular lattice in delafossites was questioned recently. A new model for understanding the magnetic properties of copper ferrite was proposed in [25] which differs significantly from the generally accepted two-dimensional Ising model. The analysis of magnetic susceptibility, magnetization and specific heat data on $CuFeO_2$ single crystals suggest a Heisenberg model with a relatively weak anisotropy to be proposed. The estimations for the main exchange interaction parameter J and the magnetocrystalline anisotropy D indicate that these two values differ by two orders of magnitude. It was suggested that besides the set of intralayer exchange interactions, the interlayer exchange interactions are crucial for the formation of the magnetic order in delafossites. Since the value of the critical field of the first metamagnetic phase transition in $AgFeO_2$ is of the same order of magnitude as the respective value in $CuFeO_2$ the analysis given for the latter compound could be applicable to the silver ferrite, too.

5. Conclusion

A study of the thermodynamic properties and neutron scattering characterization were performed on silver ferrite $AgFeO_2$. It was found, that the magnetic ordering in this compound takes place via two successive phase transitions at $T_2 = 7$ K and $T_1 = 16$ K. Unlike the case of the 'classical' delafossite $CuFeO_2$ the wavevector of the magnetic structure in the range $T_2 < T < T_1$ is independent of temperature. At $T < T_2$, the changes of slope in the magnetization curve at 14 and 30 T evidence the metamagnetic phase transitions, roughly corresponding to 1/8 and 1/4 of saturation magnetization. In general, the silver ferrite appears to be a more frustrated system with higher values of exchange interaction parameters as compared to the copper ferrite.

Acknowledgments

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