Spin-glass behavior of warwickite $MgFeBO_4$ and $CoFeBO_4$ crystals observed by Mössbauer spectroscopy

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ABSTRACT

Single crystals of $MgFeBO_4$ and $CoFeBO_4$ warwickites were obtained. The effects of charge ordering and magnetic properties were investigated by Mössbauer spectroscopy. Cation distribution over M1 and M2 nonequivalent sites and the average charge at the metal positions were established. Low temperature Mössbauer spectra reveal spin-glass behavior, with spin-freezing temperatures T_{SG} of 15.2 and 33.2 K for Mg- and Co-warwickites, respectively, higher than that observed from the d.c. and a.c. magnetic susceptibility measurements. The difference is explained in terms of dynamical scaling theory. The specific shape of the Mössbauer spectra in the vicinity of the magnetic transition at T_{SG} shows the difference between spin-glass and superparamagnetic behavior and demonstrates an overwhelming role of the exchange anisotropy in the properties of Mg-warwickite. In Co-warwickite the increase of magnetocrystalline anisotropy provokes an increase in magnetic viscosity.

1. Introduction

Homometallic and heterometallic oxyborates with one or several transition metal ions have been intensively investigated because of their rich variety of structural and magnetic properties. We have recently studied the effect of Co substitution in the phase transitions that take place in the $Fe_3O_2BO_3$ oxyborates [1]. A key tool to determine the preferential occupation of the different valent Fe(II) and Fe(III) was the low temperature Mössbauer spectroscopy (MS) experiments. In this paper MS is applied to the $MgFeBO_4$ oxyborate and its Co substituted system $CoFeBO_4$ warwickites.

Oxyborates with a general formula $M^{2+}M^{3+}BO_4$, where M^{2+} and M^{3+} are metallic ions, crystallize in the structure of mineral warwickite and have orthorhombic symmetry, space group $Pnma$ (62) (Fig. 1a and b). The low-dimensional structural units "ribbons" consist of an array of two non-equivalent octahedral sites occupied by divalent or trivalent metal ions (Fig. 1b).

The most numerous oxyborates are warwickites where M^{2+} cation is Mg^{2+} and M^{3+} is Ti, V, Cr, Mn, Fe, Ga, Sc [2,3]. Iron ions in the heterometallic warwickites are mainly in the trivalent state,

and bivalent cations may be $M^{2+} = Mn^{2+}$, Ni^{2+}, Cu^{2+}, Co^{2+}, Mg^{2+} [4–8]. Only two homometallic warwickites Fe_2BO_4 and Mn_2BO_4 which have a long-range magnetic order and undergo the antiferromagnetic transition at temperatures $T_N = 155$ and 26 K, respectively, are known [9–11]. A considerable decrease in the T_N value of Mn-warwickite is associated with high magnetic frustrations caused by almost hexagonal ordering of magnetic ions in the ribbons [12]. Both homometallic warwickites show charge ordering whose nature is actively discussed in the literature [10,13–16]. Recent studies of Fe_2BO_4 by neutron and X-ray diffraction as well as by high resolution transmission electron microscopy (HRTEM) found an incommensurate structural modulation occurring below the charge ordering transition temperature $T_{CO} = 340$ K in the range of $280 < T < 340$ K [13,16]. Fe^{2+}/Fe^{3+} ions are distributed along the a-axis in a strictly defined order, whereas the incommensurate order of antiphase stripes takes place along the c-axis, and its periodicity strongly depends on temperature [13,16]. In a recent high pressure Mössbauer spectroscopy (MS) study on Fe_2BO_4 it was shown that a strong interplay between charge ordering and magnetism takes place, with an electronic phase transition boundary at $P \approx 16$ GP [17].
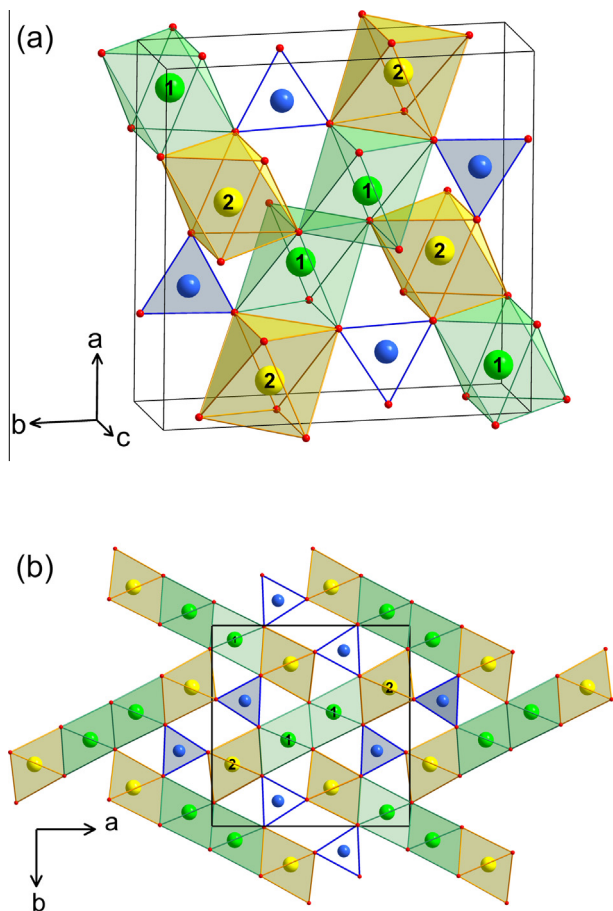
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Fig. 1. Schematic view of the warwickite $M^{2+}M^{3+}BO_4$ crystal structure. Two distorted oxygen octahedra form crystallographic sites for metal ions M1 and M2 [green and yellow balls, respectively (a)]. The boron atom sites have trigonal oxygen coordination. As seen in the *ab* plane projection (b), the M1 and M2 octahedra are linked by edges sharing in sequence 2–1–1–2 and form flat ribbons. The planar trigonal borate group (BO_3) are located in the voids between the ribbons (blue balls). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

As for the magnetic properties, the overwhelming majority of heterometallic warwickites show a transition to a spin-glass state at relatively low temperatures $T_{SG} \approx (2.7–22)$ K. In particular, the T_{SG} value for $MgFeBO_4$ was established in the range of 6–11 K [7,18], and the Mössbauer spectra indicate a strong spin relaxation in $MgFeBO_4$ near the magnetic transition. Only one report is published where the transition to a spin-glass state in $CoFeBO_4$ was found at $T_{SG} \approx 30$ K [4]. Recently, we have performed the crystal structure [19], magnetic [20] and electronic [21] studies of $MgFeBO_4$, $Mg_{0.5}Co_{0.5}FeBO_4$ and $CoFeBO_4$ single crystals. It has been shown that zero field cooled and field cooled magnetization measurements diverge below T_{SG}, in both compounds. Moreover, while $MgFeBO_4$ is isotropic, the substitution of Mg by Co introduces axial anisotropy along the *b* axis in $CoFeBO_4$ and increases the spin-glass transition temperature from $T_{SG} = 10$ K to 22 K. Frequency dependence of T_{SG}, as obtained from a.c. magnetic susceptibility, also indicates a spin-glass behavior.

In this paper, the results of investigation of the magnetic properties and the effects of charge ordering, obtained by Mössbauer spectroscopy in two heterometallic warwickites $MgFeBO_4$ and $CoFeBO_4$, are presented.

2. Experimental procedure

The flux method was employed to obtain single crystals of $MgFeBO_4$ and $CoFeBO_4$ by spontaneous crystallization from the solution – melt in the $Bi_2Mo_3O_{12}$–B_2O_3–CoO–MgO–Fe_2O_3 system. The details of synthesis and careful study of the

crystal structure and composition are given in Ref. [19]. At room temperature both samples have orthorhombic symmetry (space group *Pnma*). When replacing Mg-ions by Co-ions the unit cell parameters are slightly elongated along the *c* axis while they are shortened along the *a* and *b* axes:

a = 9.2795 Å, b = 9.4225 Å, c = 3.1146 Å, V = 272.33 Å³ for $MgFeBO_4$ and
a = 9.2144 Å, b = 9.3651 Å, c = 3.1202 Å, V = 269.25 Å³ for $CoFeBO_4$.

For the Mössbauer measurements the single crystals were ground in an agate mortar. The Mössbauer absorption spectra of ^{57}Fe nuclei were recorded in the temperature range between 5 and 295 K with a standard MS-1104Em spectrometer operating in the constant accelerations regime. The low-temperature measurements were carried out with a closed cycle helium cryostat specially developed for the Mössbauer spectrometer [22]. The gamma-ray source $^{57}Co(Rh)$ was at room temperature. The isomer shifts of Mössbauer spectra were measured relative to a metal α-Fe standard absorber (a foil 18 μm in thickness annealed in a hydrogen atmosphere). The spectra have been fitted with the Univem MS code included in the package of the MS-1104Em spectrometer. The hyperfine parameters were obtained by a least-square procedure assuming Lorentzian line shapes.

3. The room temperature Mössbauer spectra

3.1. $MgFeBO_4$

At room temperature the Mössbauer spectrum of $MgFeBO_4$ consists of an intensive doublet and a low intensity line in the right spectrum wing (Fig. 2a). The lines of the main doublet are broadened and slightly asymmetric. The minimum least-square fitting procedure indicates that this component is well approximated by two doublets D1 and D2 with close values of isomer shifts IS = 0.37 and 0.39 mm/s but with a great difference in the quadrupole splitting QS = 0.91 and 0.59 mm/s, respectively (see Table 1). These parameters are characteristic of the high spin iron ions Fe^{3+} in the paramagnetic state. The low intensity line belongs to the third quadrupole doublet D3 (see Fig. 2(a)) with the parameters IS = 1.18 mm/s and QS = 2.08 mm/s, which identify the Fe^{2+} ions in the high-spin paramagnetic state. The area S of this component is about 2% of all iron in the sample, and this line can belong to either Fe^{2+} impurity ions in interstitial sites of warwickite lattice or Fe^{2+} ions in oxygen octahedra of the basic lattice.

The areas of the main doublets D1 and D2 [the iron occupation factor] are about 57% and 41%, respectively, and it is reasonable to assign these doublets to crystallographically nonequivalent sites M1 and M2 in the warwickite structure [19]. The electric field gradient V_{zz} (EFG) of the M1 site is higher than the M2 site in both $MgFeBO_4$ and $CoFeBO_4$ compounds. This indicates that the oxygen $M1O_6$ octahedra are more distorted than the $M2O_6$ octahedra. Therefore, the D1 doublet with a greater QS value should be assigned to the Fe^{3+} ions in the M1 sites. This means that the occupation of M1 sites in $MgFeBO_4$ by Fe^{3+} ions is greater than that of M2 sites. Since the main part of Mg^{2+} ions (about 60%) occupies the M2 sites, we can assume that Fe^{2+} ions also prefer the M2 sites. Then, as deduced from the Mössbauer data, the cation distribution in $MgFeBO_4$ can be written as $(Fe^{3+}_{0.57} Mg^{2+}_{0.43})^{M1} (Fe^{3+}_{0.41} Fe^{2+}_{0.02} Mg^{2+}_{0.57})^{M2} B^{3+} O^{2-}_4$. In this case, the average cation valence in the M1 and M2 sites is 2.57 and 2.41, respectively [i.e. the average formal charge at the M1 and M2 metal positions]. The obtained values are in a good agreement with the results of bond valence calculation (2.54 and 2.26) [19].

3.2. $CoFeBO_4$

The shape of the Mössbauer spectrum for $CoFeBO_4$ at room temperature is analogous to that for Mg-warwickite (Fig. 2b). The spectrum is also well approximated by three doublets D1, D2, and D3, from which D3 belongs to a small amount (about 2%) of Fe^{2+} ions. The values of IS and QS for D1 and D2 components in a $CoFeBO_4$ crystal are typical of high-spin states of Fe^{3+} ions (see Table 1). It follows from these data that to retain the electric neutrality of
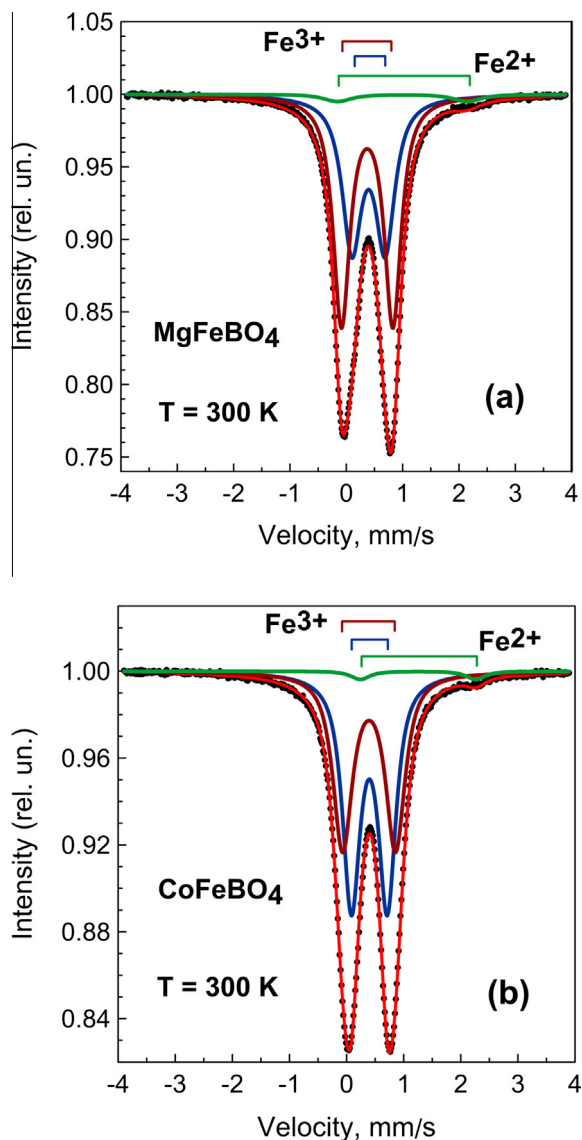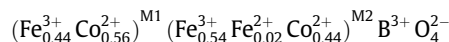
Fig. 2. Room temperature Mössbauer spectra of (a) MgFeBO$_4$ and (b) CoFeBO$_4$. The two main solid lines are the calculated spectrum components corresponding to the M1 and M2 sites of Fe^{3+} ions in warwickites. The third small-intensity line corresponds to Fe^{2+} ions.

molecule, the cobalt ions in warwickite should be bivalent Co^{2+}-Fe^{3+}B^{3+}O$_4^{2-}$. The areas of the main doublets [the iron occupation factor] D1 and D2 belonging to Fe^{3+} ions in M1 and M2 sites of CoFeBO$_4$ are 44% and 54%, respectively. This shows that, contrary to Mg-warwickite, the occupation of M1 positions by Fe^{3+} in Co-warwickite is less than that of M2 positions.

Considering that Fe^{2+} ions prefer the M2 sites (analogous to Mg^{2+} ions), based on the Mössbauer data, a cation distribution in CoFeBO$_4$ can be written as:

$$(Fe_{0.44}^{3+} Co_{0.56}^{2+})^{M1} (Fe_{0.54}^{3+} Fe_{0.02}^{2+} Co_{0.44}^{2+})^{M2} B^{3+} O_4^{2-}$$

In this case the average valence (charges) of cations in the M1 and M2 sites is 2.44 and 2.54, respectively [the average formal charge at the M1 and M2 metal positions].

4. Low temperature Mössbauer data

At low temperatures the Mössbauer spectra of MgFeBO$_4$ and CoFeBO$_4$ are split into six Zeeman components indicating the magnetic ordering of iron ions (Fig. 3a and b). It is significant that even at the lowest temperature of this experiment (5 K) the first and sixth lines of the spectrum of both samples are noticeably broadened into the internal part of the spectra, which indicates a non-uniform magnetic state. An analysis in terms of distribution functions for magnetic hyperfine fields did not show any splitting into distinct components. In fact, its shape was the same as for the 1st and 6th lines of the spectra at 5 K. Instead, we show below that the spectra at 5 K can be reasonably well approximated by three sextets with close values of the isomer shift IS and the quadrupole shift ε [23], but a different value of the magnetic hyperfine field H_{hf} at the iron nuclei (Fig. 4a and b). It turned out that at 5 K the values of H_{hf} in MgFeBO$_4$ are considerably lower (by 3.0–3.4 T) than in CoFeBO$_4$ (Table 2). Fairly wide lines of three fitted sextets indicate a significant field distribution within the limits of 44.7–36.5 T for the Mg-sample and 47.6–40.0 T for the Co-sample.

We found that the areas of the components with the maximum value of field H_{hf} = 44.7 and 47.6 T for Mg- and Co-samples, respectively, prove to be equal to the occupation of M2 sites by Fe^{3+} ions obtained from the Mössbauer spectra of both samples in the paramagnetic region (see Tables 1 and 2). This indicates that the H_{hf} value in M2 sites is significantly higher than that in M1 sites. In addition, the distribution of H_{hf} in sites M1 is much broader than in sites M2.

It is important to note that the highest values of H_{hf} in both Mg- and Co-samples prove to be much less than the field typical of Fe^{3+} ions at the octahedral sites in oxides (about 55.0 T). These specific features indicate an unusual magnetic state of iron sublattice. Apparently, the magnetization vector fluctuates near the easy magnetization axis due to frustration of magnetic interactions, which leads to a decrease of H_{hf}.

When temperature rises, in both MgFeBO$_4$ and CoFeBO$_4$ compounds the magnetic splitting of the spectra lines gradually decreases, and the outer lines (1-th and 6-th lines) broaden into the internal part of spectra (Fig. 3). At the same time, two internal lines (3-th and 4-th) are almost not broadened. For example, a typical doublet is observed in the center of the CoFeBO$_4$ spectrum at 29 K, whose parameters are different from those of the paramag-
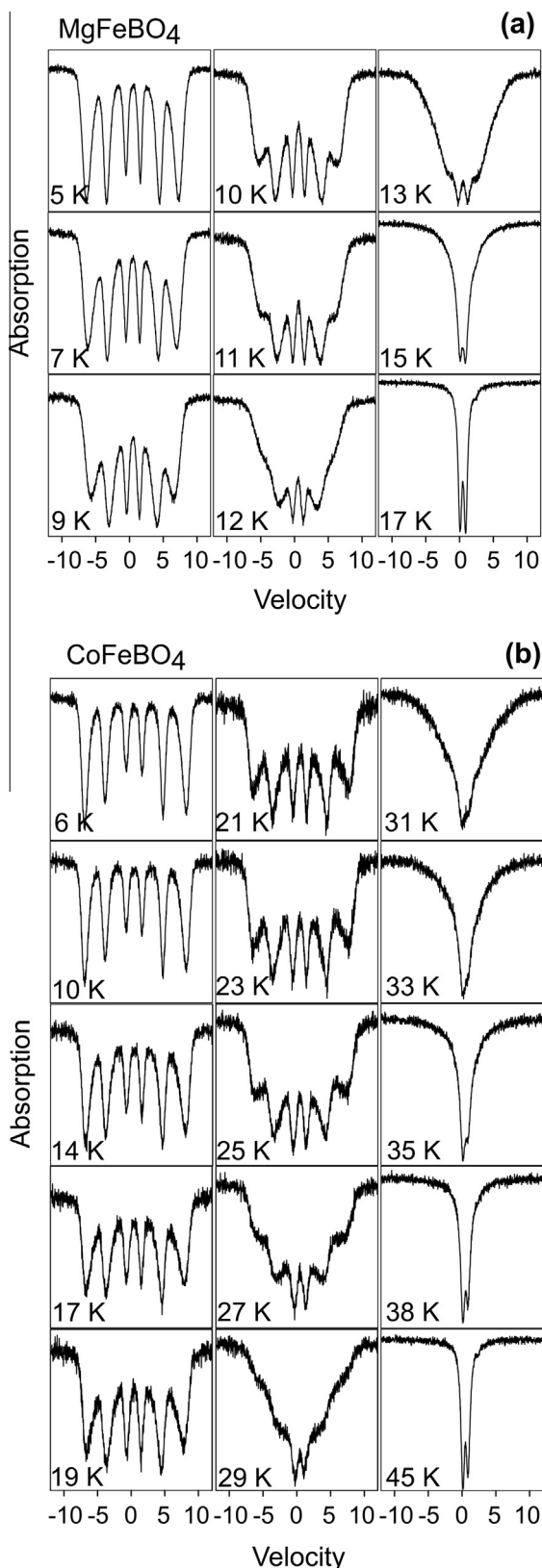
Table 1
Hyperfine parameters obtained from the room-temperature Mössbauer spectra of CoFeBO$_4$ and MgFeBO$_4$. IS is the isomer shift relative to α-Fe (±0.01 mm/s), QS is the quadruple splitting (±0.01 mm/s), Γ is the half-line width (±0.01 mm/s), and S is the area of the corresponding component (±1.5%) [the iron occupation factor].

	IS (mm/s)	QS (mm/s)	Γ (mm/s)	S (%)	Fe site	Fe valence	Average formal charge
MgFeBO$_4$							
D1	0.37	0.91	0.36	57.2	M1	+3	2.57
D2	0.39	0.59	0.41	40.8	M2	+3	2.41
D3	1.18	2.08	0.42	2	M2	+2	2.0
CoFeBO$_4$							
D1	0.39	0.93	0.41	44	M1	+3	2.44
D2	0.40	0.63	0.37	54	M2	+3	2.54
D3	1.25	2.02	0.40	2	M2	+2	2.0

Fig. 3. Representative Mössbauer spectra of warwickites (a) MgFeBO$_4$ and (b) CoFeBO$_4$ in the temperature region of magnetic transition.

Fig. 4. Low temperature Mössbauer spectra of (a) MgFeBO$_4$ and (b) CoFeBO$_4$. Three solid lines indicate the calculated spectrum components which hyperfine parameters are given in Table 2.

netic doublet at 300 K. This fact indicates a magnetic nature of the central doublet at 29 K. Such behavior of Mössbauer spectra differs from that for superparamagnetism and is typical of frustrated state
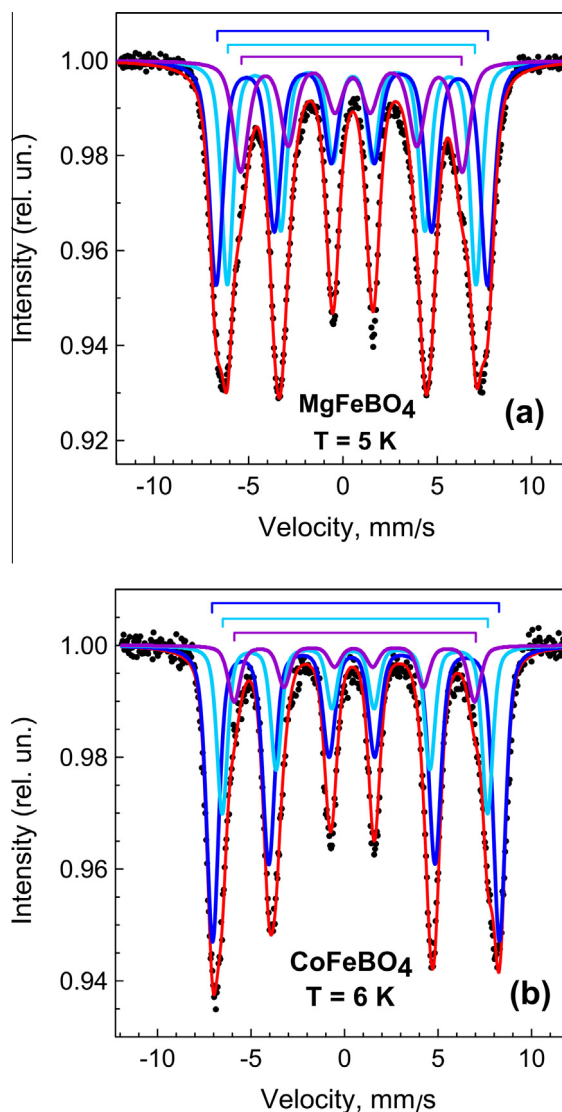
of the iron magnetic moments, which is a feature of spin-glass [24,25]. The line broadening in spin-glass occurs because of fluctuations of the exchange anisotropy constant K_{ex} (see below), which differs for the ions in M1 and M2 sites due to the different nearest environment of these sites by Fe and Co ions.

The mean value of hyperfine magnetic field $\langle H_{hf} \rangle$ has been calculated from the distance between any two spectral line of the six-line spectrum. When spectral lines are broadened, $\langle H_{hf} \rangle$ value has been calculated from the positions of the maxima of the widened lines. When all six lines overlap, the $\langle H_{hf} \rangle$ value has been estimated from the total width of the spectrum. In our study we used the three methods in the different temperature ranges. We have plotted the temperature dependence of the average value of magnetic field $\langle H_{hf} \rangle$ (Fig. 5) and determined the temperature of spin "freezing" T_{SG} (transition to a spin-glass state): T_{SG} = 15.3 K and T_{SG} = 33.1 K for MgFeBO$_4$ and CoFeBO$_4$, respectively. These values are obtained by the extrapolation of $\langle H_{hf} \rangle$ to zero value. However, the remanent line broadening of magnetic nature is still seen at 17 K in the MgFeBO$_4$ and at 35 K in the CoFeBO$_4$ spectra (Fig. 3). This indicates the presence of magnetic correlations at temperatures above T_{SG}, and the transition to the paramagnetic state is gradually extended to higher temperatures.

Table 2
Hyperfine parameters obtained from the low-temperature (5 K) Mössbauer spectra of MgFeBO$_4$ and CoFeBO$_4$. H_{hf} is the magnetic hyperfine field at Fe nuclei ($\pm$0.05 T), IS is the isomer shift relative to α-Fe ($\pm$0.01 mm/s), ε is the quadruple shift ($\pm$0.01 mm/s), Γ is the half-line width ($\pm$0.05 mm/s), and S is the area of the corresponding component ($\pm$1.5%) [the iron occupation factor].

	H_{hf} (T)	IS (mm/s)	ε (mm/s)	Γ (mm/s)	S (%)	Site/valence
MgFeBO$_4$						
1	44.67	0.50	−0.06	0.86	41.6	M2/Fe^{3+}
2	40.93	0.50	−0.06	0.75	35.7	M1/Fe^{3+}
3	36.47	0.48	−0.06	0.96	22.7	M1/Fe^{3+}
CoFeBO$_4$						
1	47.61	0.50	0.22	0.78	59.2	M2/Fe^{3+}
2	44.01	0.50	0.10	0.68	29.5	M1/Fe^{3+}
3	39.91	0.51	0.04	0.78	11.3	M1/Fe^{3+}

As seen in Fig. 5, the $\langle H_{hf}\rangle(T)$ curve for MgFeBO$_4$ does not reach saturation with decreasing temperature down to the lowest temperatures which indicates that iron spin fluctuations still remain at 5 K. This implies that the exchange anisotropy is not high enough to freeze the spin fluctuations. In contrast, in CoFeBO$_4$ the saturation is achieved at $T < 15$ K which indicates that the fluctuations in the spin direction are essentially suppressed. This can be explained by the additional contribution of magnetocrystalline anisotropy which is induced by the Co ions.

5. Discussion

According to theory [26–29], the spin-glass state can appear when the exchange interactions between the spins (atoms) in the matrix oscillate in value and sign depending of the distance between the interacting atoms. In that case, there is no ferro- or antiferromagnetism in a crystal on average, however, the ground state permits local spin alignment in a definite direction, although these directions occur chaotically.

Unlike magnetic measurements, whose time is comparatively large (10^{-4}–100 s), the characteristic time in the Mössbauer experiment is about 10^{-9} s, therefore, the ^{57}Fe nuclei can monitor faster processes of magnetic fluctuations which lead to zero averaging of magnetization for a longer measuring time.

Note that the T_{SG} values found from our Mössbauer studies are noticeably higher than those obtained from the measurements of d.c. magnetic susceptibility ($T_{SG} = 10$ K for MgFeBO$_4$ and $T_{SG} = 22$ K for CoFeBO$_4$ [20]). Such a larger value of the "Mössbauer transition temperature" with respect to T_{SG} as determined from suscep-

Fig. 5. Temperature dependence of the average value of magnetic hyperfine field $\langle H_{hf}\rangle$ at iron nuclei obtained from the Mössbauer spectra of MgFeBO$_4$ and CoFeBO$_4$. Dash lines near T_{SG} are calculated curves obtained by the approximation Eq. (4) and at low temperatures by Eq. (5).

tibility (by $\approx$30%), is explained by the deviation of the spin-glass relaxation time τ_M from the paramagnetic value ($\approx 10^{-12}$ s) already at $T > T_{SG}$ [29]. Indeed, in the magnetic relaxation study [20] the Dynamical scaling theory was applied to obtain a fit of the frequency dependence of the maximum in the a.c. susceptibility $T(\omega)$:

$$f = f_0 \left[\frac{T(\omega)}{T_c} - 1\right]^{zv}, \tag{1}$$

where $T(\omega)$ is the spin-glass transition temperature as a function of the frequency, T_c is the phase transition temperature in the limit of zero frequency and zv is the dynamical exponent [30]. For MgFeBO$_4$ and CoFeBO$_4$ the parameter values $T_c = 11$ and 20.4 K, $f_0 = 3.0 \times 10^9$ and 1.2×10^{12} Hz, and $zv = 5$ and 14, respectively, were obtained from the fits of the scaling law [20]. Now, with these parameters, and at the characteristic frequency of the MS experiment; i.e. for the Larmor frequency $f = f_L = 2.2 \times 10^8$ Hz, calculated for $H_{hf} \approx 50$ T, by substitution in Eq. (1), the predicted values are $T(\omega_L) = 17.5$ and 31.4 K, respectively, in excellent agreement with the experimental $T_{SG} = 15.3$ and 33.1 K deduced from the present MS experiment. Thus, the Dynamical Scaling theory is fulfilled by the spin-glass behavior of these compounds.

The influence of the relaxation processes on Mössbauer spectra in the spin-glass resembles the processes observed in superparamagnets [24,25]. The exchange interaction energy of the iron atom in the position i with the nearest atoms in the position j can be described by the expression [24]

$$E_i = -\sum_{j=1}^{z} K_{ex}^{ij} m_i \cdot m_j \tag{2}$$

where m_i and m_j are the magnetic moments of atoms in the positions i and j, z is the number of atoms interacting with the atom i, and K_{ex}^{ij} is exchange interaction constant between these atoms. Within a mean field model applied to Eq. (2) the parameter $K_{ex} = \sum_{j=1}^{z} K_{ex}^{ij}$ is defined as the exchange anisotropy energy constant. Because of the fluctuations in the direction of magnetic moments K_{ex} can be described in terms of its average value, K_{ex}^0, and the standard deviation K_{ex}^d. In the case of $K_{ex}^d \geq K_{ex}^0$ i.e. when its fluctuations are of the order of the average exchange anisotropy constant, the spin-glass behavior is followed. The "frozen" magnetic moment q, that is the parameter of spin-glass theory, is associated with the Mössbauer value H_{hf}:

$$q^{1/2}(T) = \left(\left\langle \langle m_i\rangle^2 \right\rangle_d\right)^{1/2} \tag{3}$$

where $\langle\ldots\rangle_d$ is the average value over all magnetic moments m_i and $\langle\ldots\rangle$ is the value of moment averaged over the time which is considerably larger than the correlation time τ of the fluctuations of magnetic moment directions [24]. Below T_{SG} $\langle m_i\rangle^2 \neq 0$, and $\langle\langle m_i\rangle\rangle_d = 0$. If τ is shorter than the Mössbauer time (i.e., the time of the Larmor precession of ^{57}Fe nuclei magnetic moment in the field H_{hf}), the average field $\langle H_{hf}\rangle_d$ is proportional to $q^{1/2}(T)$. Then the temperature dependence of field $\langle H_{hf}\rangle_d$ should be qualitatively similar to $q^{1/2}(T)$. Thus, at T a little lower than T_{SG} the field should be proportional to

$$\langle H_{hf}/H_0\rangle_d \propto (T_{SG} - T)^{\beta}, \tag{4}$$

with $\beta = 1/2$. Moreover, the field is linearly dependent on T at $T \ll T_{SG}$. [H_0 is the H_{hf} value at $T = 0$]. The critical exponent $\beta = 1/2$ is characteristic of short range spin-glasses, with frustration as the main mechanism to generate the magnetic moment direction fluctuations [30]. Under this assumption, we have fitted experimental values of $\langle H_{hf}\rangle$ with Eq. (4) and found $T_{SG} = 15.2$ and 33.2 K for Mg- and Co-warwickites, respectively. These values practically coincide with the values found above from a simple linear extrapolation just below T_{SG}.
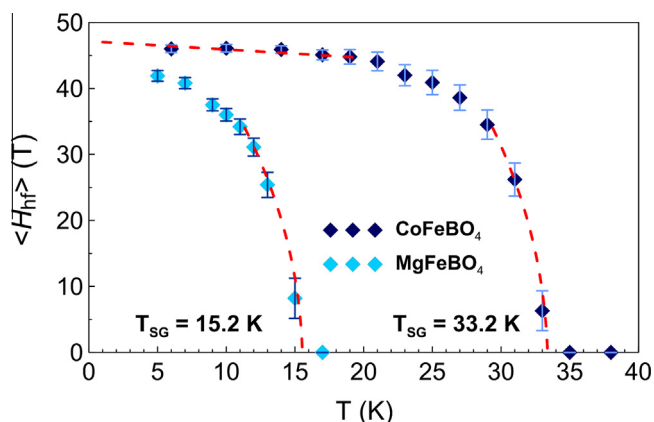
As a conclusion from all the results and analysis, Mg-warwickite shows "ideal" properties of the spin-glass. This suggests that the exchange anisotropy prevails and determines the properties of this crystal.

Within the model described above, at low temperature the linear dependence of H_{hf} with temperature is predicted [24]:

$$\left\langle \frac{H_{hf}}{H_0} \right\rangle \approx (1 - AT), \text{ with } A = \frac{k_B}{\langle E_{anis} \rangle}. \tag{5}$$

Here $E_{anis} = E_{ex} + E_{cryst}$, where E_{ex} is the exchange anisotropy energy described in Eq. (2), and E_{cryst} corresponds to any other sources of anisotropy, for example, magnetocrystalline anisotropy.

If one applies Eq. (5) to the value of fitted slope for the CoFeBO$_4$ below 20 K one obtains $A = 2.67 \times 10^{-3}$ K^{-1}, and $\langle E_{anis} \rangle/k_B = 370$ K. In contrast, the slope of the tangent to the curve for MgFeBO$_4$ has the value $A \leqslant 1.5 \times 10^{-2}$ K^{-1}, and consequently $\langle E_{anis} \rangle/k_B = \langle E_{ex} \rangle/k_B \geqslant 66$ K where any magnetocrystalline anisotropy has been neglected since this compound is isotropic. Using the expression $\langle E_{ex} \rangle = 2z\langle J_j \rangle(S(S+1))$, for $S = 5/2$ and $z = 2$, we obtain $\langle |J_j| \rangle/k_B = 1.9$ K, which is quite comparable to the values of exchange interaction parameters J_j calculated for MgFeBO$_4$ (see Table V in Ref. [20]). One concludes that the difference in E_{anis} between the MgFeBO$_4$ and CoFeBO$_4$ can be ascribed, therefore, to an increase in the exchange anisotropy energy in the latter, because of an increased value of the exchange constants J_j due to Co substitution (see Ref. [20]), and to the significant crystalline anisotropy induced by Co^{2+} ions, which are known to have a strong orbital moment.

In short, if the correlation time of fluctuations of the magnetic moment directions is small compared with the Mössbauer time, then H_{hf} can take any values in the range $0 < H_{hf} < H_0$ depending on the temperature and the value of exchange coupling. The distribution of exchange anisotropy constants K_{ex} may lead to a wide H_{hf} distribution. This distribution of H_{hf} and the absence of paramagnetic components in the Mössbauer spectra at $T < T_{SG}$ are robust arguments indicating an overwhelming role of exchange anisotropy in the properties of the MgFeBO$_4$ warwickite crystals, and classify it as an "ideal" spin-glass. In contrast, in CoFeBO$_4$ the increase in magnetocrystalline anisotropy along the b axis, as observed in the magnetization measurements (Ref. [20]), suppress the fluctuations in spin direction and, as a consequence, complete freezing of the of the spins is achieved at temperatures below 15 K.

Acknowledgments

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